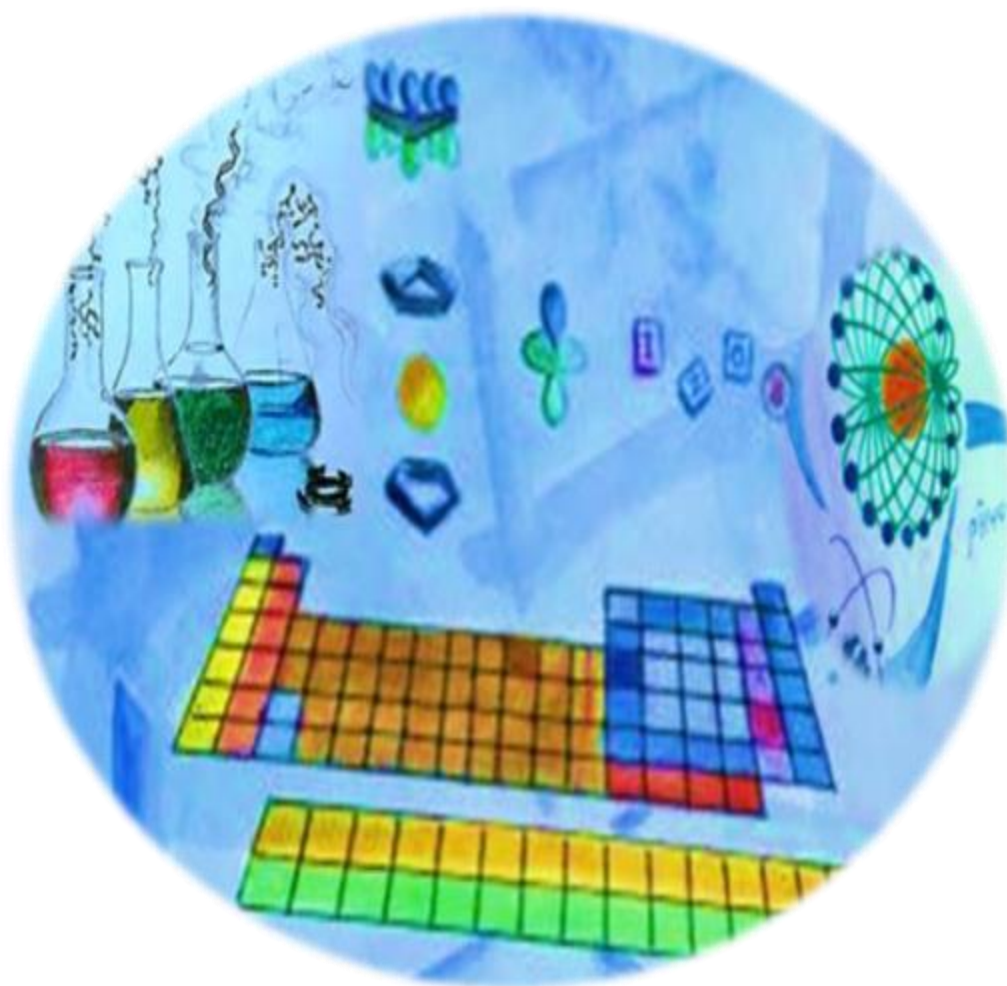




IIT Bombay Diamond Jubilee Chemistry Symposium



**Venue: VMCC
Date: February 25-28, 2019**

February 25, 2019 (Monday); Venue: B. Nag Auditorium, VMCC

Time	Event	Speaker	Venue
8:30 – 9:00 h	Registration		
9.00 – 9.30 h	Inauguration	Chief Guest: Prof. A. K. Suresh Deputy Director (AIA)	Prof. B. Nag Auditorium
Chair: Prof. S. Chandrasekharan			
9.30 – 10.00 h	Autonomous Chemistry for Reaction Optimization and the Production of Affordable Drugs Prof. Peter Seeberger		
10.00 – 10.30 h	Synthesis of Hentriacontahectanosyl Arabinogalactan Present in the Cell Wall of Mycobacterium tuberculosis by Gold-catalyzed Glycosidations Prof. S. Hotha		
10.30 – 11.00 h	Designing of templates to reach the distal C-H bond Prof. Debabrata Maiti		
11.00 – 11.30 h	Tea		
Chair: Prof. H. B. Singh			
11.30 – 12.00 h	Iodine in Thyroid Hormone Action and Membrane Transport Prof. G. Mugesh		
12.00 – 12.30 h	A Liquid Crucible Model for Formation of Polymorphs Prof. G. Naresh Patwari		
12.30 – 13.00 h	Topological Effects on Movements of Charged Macromolecules in Crowds Prof. M. Muthukumar		
13.00 – 14.30 h	Lunch		
Chair: Prof. Amitava Chattopadhyay			
14.30 – 15.00 h	Photoluminescence and Ultrafast Dynamics of All-Inorganic Perovskite Nanocrystals Prof. Anunay Samanta		
15.00 – 15.30 h	Towards Non-Equilibrium Supramolecular Polymers Prof. Subi George		
15.30 – 16.00 h	Looking out for Green tea polyphenols Prof. Swagata Dasgupta		
16.00 – 16.30 h	Tea		
Chair: Prof. Bhalchandra Bhanage			
16.30 – 17.00 h	Using operand Raman spectro-electrochemistry to understand support-catalyst-electrolyte interface and interplay in alkaline hydrogen evolution reaction Prof. C. Subramaniam		
17.00 – 17.30 h	“De Novo Oligosaccharide Synthesis and Medicinal Chemistry: Use of the Taylor catalyst in a Pd/B-catalyzed Abiotic Glycosyl-Transferase” Prof. George O’Doherty		
17.30 – 18.00 h	Total Synthesis Driven Methodologies Prof. C. V. Ramana		

February 26, 2019 (Tuesday); Venue: B. Nag Auditorium, VMCC

Time	Speaker
Chair: Prof. Sourav Pal	
9.30 – 10.00 h	Molecular Magnets as MultiFerroic Materials Prof. G. Rajaraman
10.00 – 10.30 h	Transition Metal-Free C-C Coupling Catalysis Prof. Swadhin Mandal
10.30 – 11.00 h	Molecules or Molecular assemblies for Predictive Responses Prof. Amitava Das
11.00 – 11.30 h	Tea
Chair: Prof. R. V. Hosur	
11.30 – 12.00 h	Enantioselective Conjugate Addition Reactions Prof. Vinod K. Singh
12.00 – 12.30 h	Computations $\longleftrightarrow$ Experiments Challenges in Synergizing Asymmetric Catalysis Prof. R. B. Sunoj
12.30 – 13.00 h	Exocyclic olefinic maleimides as versatile scaffolds for bioconjugation Prof. Dimpy Kalia
13.00 – 14.30 h	Lunch and Poster Session (P1-P22)
Chair: Prof. C. P. Rao	
14.30 – 15.00 h	Indoleamine-2,3-dioxygenase (IDO) Inhibition as a strategy to Augment Cancer Immunotherapy Prof. Debasis Manna
15.00 – 15.30 h	Singlet Exciton Fission in Conjugated Organic Molecules Prof. Jyotishman Dasgupta
15.30 – 16.00 h	Single Molecule Switching and Sensing Prof. Eric Borguet
16.00 – 16.30 h	Tea
Chair: Prof. A. K. Singh	
16.30 – 17.00 h	Diverted Total Synthesis: From Macrolactones to Alkaloids Prof. K. R. Prasad
17.00 – 17.30 h	Development of New Synthetic Strategies and Tactics: Their Impact, Implications, and Applications Prof. S. R. Kotha
17.30 – 18.00 h	Propargylic Alcohols in Annulation Reactions: Recent Endeavors Prof. Raji Reddy

February 27, 2019 (Wednesday); Venue: Room 31, 3rd floor, VMCC

Time	Speaker
Chair: Prof. Swapan Ghosh	
9.30 – 10.00 h	Reactivity of Main-Group Compounds Containing Double Bonds <i>Prof. V. Chandrasekhar</i>
10.00 – 10.30 h	Redox-Active Mesoionic Carbenes for Redox-Switchable Catalysis <i>Prof. Biprajit Sarkar</i>
10.30 – 11.00 h	Structural modification in reverse micelles and growth of anisotropic nanostructures <i>Prof. Ashok Ganguli</i>
11.00 – 11.30 h	Tea
Chair: Prof. S. N. Datta	
11.30 – 12.00 h	Photoprotection pathways in human skin pigment eumelanin <i>Prof. Debasree Ghosh</i>
12.00 – 12.30 h	Hybrid Quantum-Classical Studies of an Enzymatic Reaction in Aqueous Medium <i>Prof. Amalendu Chandra</i>
12.30 – 13.00 h	Targeting structure specific DNAs and Proteins for therapeutic and sensor applications <i>Prof. A. C. Bhasikuttan</i>
13.00 – 14.30 h	Lunch and Poster Session (P23-P44)
Chair: Prof. A. Q. Contractor	
14.30-15.00 h	The Tale of Two Tetrellylenes for Cu(I)- and Au(I)-Arene Complexes <i>Prof. Shabana Khan</i>
15.00 – 15.30 h	Investigation of Novel Nano-structures for the Methanol Oxidation Reaction <i>Prof. Santosh Haram</i>
15.30 – 16.00 h	Emergence of Chiral Structures in Lyotropic Liquid Crystals <i>Prof. Mohan Srinivasarao</i>
16.00 – 16.30 h	Tea
Chair: Prof. A. V. Karnik	
16.30 – 17.00 h	Synthesis of Biopolymer Mimics via Topochemical Reactions <i>Prof. K. Sureshan</i>
17.00 – 17.30 h	Metal-Free Approaches for the Construction of Privileged Scaffolds <i>Prof. S. Ramasastry</i>
17.30 – 18.00 h	Chemical toolbox for precision engineering of proteins <i>Prof. Vishal Rai</i>

February 28, 2019 (Thursday); Venue: Room 31, 3rd floor, VMCC

Time	Speaker
Chair: Prof. B. L. Tembe	
9.30 – 10.00 h	Hydrophobic-Hydrophilic interactions in protein folding, protein-protein association and molecular recognition <i>Prof. A. Ben-Naim</i>
10.00 – 10.30 h	H-bonding Regulated Supramolecular Nanostructures and Impact on Multivalent Binding with Biological Targets <i>Prof. Suhrit Ghosh</i>
10.30 – 11.00 h	Continuous Flow Materials and Chemicals Manufacturing: A New Paradigm in Process Intensification <i>Prof. Anil Kumar</i>
11.00 – 11.30 h	Tea
Chair: Prof. Anindya Datta	
11.30 – 12.00 h	Allosteric Regulation of Transient Molecular Tunnels <i>Prof. Ruchi Anand</i>
12.00 – 13.00 h	Liquids, Crystals, Liquid Crystals, Plastic Crystals, and More ... <i>Prof. Michael L. Klein</i>
13.00 – 14.30 h	Lunch

Link for the Abstracts of Oral and Poster presentations: <https://tinyurl.com/y4hcy9ca>

Or scan this QR code



Book of Abstracts

Autonomous Chemistry for Reaction Optimization and the Production of Affordable Drugs

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Abstract:

Continuous chemical processes have attracted both academic and industrial interest. In this lecture, I will discuss our recent progress to completely autonomous chemical processes covering three topics: Initially, some new methods, particularly continuous photochemistry using solids in serial micro-batch reactors will be reported. Next, an automated reaction optimization system to study the mechanism of glycosylation reactions will be discussed. Finally, autonomous chemical systems using a radial synthesizer concept that hold the potential to fundamentally change the practice of chemical synthesis will be described.

Selected References:

1. Plutschack, M.; Pieber, B.; Gilmore, K.; Seeberger, P.H.; *Chem.Rev.***2017**, *117*, 11796.
2. Pieber, B.; Shalom, M.; Antonietti, M.; Seeberger, P.H.; Gilmore, K.; *Angew. Chem. Int. Ed.***2018**, *57*, online
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Synthesis of Hentriacontahectanosyl Arabinogalactan Present in the Cell Wall of *Mycobacterium tuberculosis* by Gold-catalyzed Glycosidations

Sandip Pasari, Mahesh Neralkar and Srinivas Hotha*

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Abstract:

Mycobacterium tuberculosis (MTb) has a thick and waxy cell wall that does not let antibiotics permeate through it. Seminal studies by Brennan during 1980-1995 unravelled the chemical structure of MTb cell wall to notice that it has four major components viz. mycolyl trehalose, arabinogalactan (AG), lipoarabinomannan (LAM) and peptidoglycan.¹ Among these, arabinogalactan is the most complicated structure containing arabinose and galactose in the furanosyl form. The reducing end of this AG is attached to the peptidoglycan through a Rhap-GlcpNAc linker disaccharide.² The fine structure of AG showed that there are 131-sugar residues out of which 93 residues are Arafs, 36 sugars are Galfs and one each of Rhap and GlcpNAc. Many therapeutically relevant molecules, including some in clinics, are found to inhibit the biosynthesis of either arabinan or galactan.¹ The complex architecture coupled with the challenge of synthesizing such oligosaccharides has attracted the attention of synthetic carbohydrate chemistry community since 1996. Several oligomers are synthesized; the most recent ones being the heneicosasaccharide of AG,^{3a,c} heneicosasaccharide of LAM,^{3b} pentacosasaccharide of AG^{3d} are from our group³ and a large 92-mer⁴ of AG by the Xin-Shan Ye group. Nevertheless, the total synthesis of full length Hentriacontahectanosyl Arabinogalactan (131-mer) has not been reported till date.

A decade long effort in our group culminated in excellent methods for the glycosylations and stereoselective synthesis of 1,2-*cis* and 1,2-*trans* furanosides under mild conditions.⁵ We have successfully demonstrated the utility of these methods for the synthesis of some of the oligosaccharides of *Mycobacterium tuberculosis* cell wall. An account of these results including our current efforts towards the synthesis of Hentriacontahectanosyl Arabinogalactan (131mer) will be presented.

References:

1. Besra, G. S.; Chatterjee, D. *In Tuberculosis: Pathogenesis, Protection and Control* (Ed.: Bloom, B. R.), American Society, Microbiology Press, Washington DC, **1994**, 285-306.
2. (a) Besra, G. S.; Khoo, K.-H.; McNeil, M. R.; Dell, A.; Morris, H. R.; Brennan, P. J. *Biochem.* **1995**, *34*, 4257-4266; (b) Brennan, P. J.; Nikaido, H. *Annu. Rev. Biochem.* **1995**, *64*, 29-453.
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Designing of templates to reach the distal C–H bond

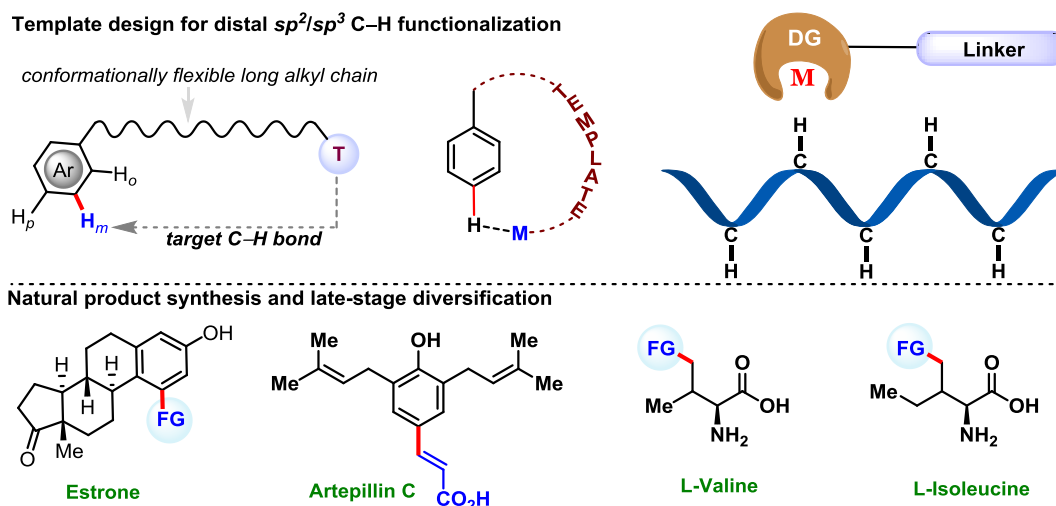
Debabrata Maiti

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Mimicking the nature has always been a coveted target for scientific communities. A precise understanding has emerged as to how enzymes accomplish the chemical transformations. Enzymes catalyze inert C–H bond functionalization in a regio- and stereoselective manner using metal-active site. Inspired by the nature, we have developed catalytic methods to functionalize carbon–hydrogen (C–H) bonds which provides significant economic and environmental benefits over traditional synthetic methods. Applicability of our strategies towards synthesis of various complex molecules will be discussed.



References

Maiti, D. and co-workers, *J. Am. Chem. Soc.* **2014**, 136, 13602; *J. Am. Chem. Soc.* **2015**, 137, 11888; *J. Am. Chem. Soc.* **2017**, 39, 763; *Angew. Chem. Int. Ed.* **2015**, 54, 8515; *Angew. Chem. Int. Ed.* **2016**, 55, 7751; *Angew. Chem. Int. Ed.* **2017**, 56, 3182; *Angew. Chem. Int. Ed.* **2017**, 56, 5272; *Angew. Chem. Int. Ed.* **2017**, 56, 12538; *Angew. Chem. Int. Ed.* **2017**, 56, 14903; *Angew. Chem. Int. Ed.* **2018**, 57, 7659; *Nature Commun.* **2018**, 9, 3582; *Chem. Sci.* **2018**, 9, 7843

Brief-Bio: Prof. Debabrata Maiti received his PhD from Johns Hopkins University (USA) in 2008 under the supervision of Prof. Kenneth D. Karlin. After postdoctoral studies at Massachusetts Institute of Technology (MIT) with Prof. Stephen L. Buchwald (2008–2010), he joined the Department of Chemistry at IIT Bombay in 2011 wherein currently he is an Associate Professor. His research interests are focused on the development of new and sustainable synthetic and catalytic methodologies. Currently he is an Associate-Editor of *Journal of Organic Chemistry*.

Iodine in Thyroid Hormone Action and Membrane Transport

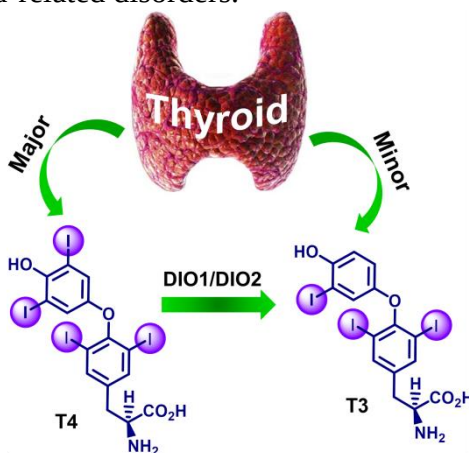
G. Mugesh

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Abstract:

Thyroid hormones regulate almost every process in the body, including body temperature, growth, and heart rate. They influence carbohydrate metabolism, protein synthesis and breakdown, and cardiovascular, renal, and brain function. The deiodination of thyroxine (T4) by iodothyronine deiodinases (DIOs) play a crucial role in thyroid hormone action. These enzymes contain selenocysteine, the 21st amino acid, in their active sites. The phenolic ring (5') deiodination of T4 by the type 1 and 2 enzymes (DIO1 and DIO2) produces the biologically active hormone, 3,5,3'-triiodothyronine (T3), whereas the tyrosyl ring (5) deiodination of T4 by the type 3 enzyme (DIO3) produces the biologically less active hormone rT3. Therefore, the complex biochemical dehalogenation pathways play an important role not only in human hormone action, but also in the development of drugs for thyroid-related disorders.



In this lecture, the chemical mechanism by which the deiodinases and organoselenium compounds selectively activate and inactivate the thyroid hormones will be discussed. The role of iodine atom and halogen bonding in the membrane transport of fluorescent molecules will also be discussed.

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A Liquid Crucible Model for Formation of Polymorphs

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Abstract:

The aggregation of molecules leading to solid state structures in many cases go through the process of liquid-like clusters, which an further form ordered array as the crystallites. The liquid-like cluster can be considered as the “crucible” or “melting pot” in the nucleation of polymorphs. Understanding the properties of these liquid-like clusters would enable us to control the polymorphs. Spectroscopic methods can be utilized to probe the formation of these liquid-like clusters. Herein, IR spectroscopic investigations on size selective clusters consisting of up to six monomer units were carried out. Analysis of the IR spectra with aid of quantum chemical calculations reveals the formation of anti-parallel π -stacked structure for dimer and structure incorporating exclusively aromatic C–H $\cdots\pi$ interactions. The aggregation behaviour of phenylacetylene in the gas phase is fundamentally different from benzene, phenol and aniline vis-à-vis their crystal structures. The structures of the three known polymorphic crystal structures can be reconciled by the formation of supramolecular synthon with acetylenic C–H $\cdots\pi$ interactions, which is preferred over energetically favored aromatic C–H $\cdots\pi$ interactions. Furthermore, the small (phenylacetylene)_n [n = 3-6] clusters incorporating aromatic C–H $\cdots\pi$ interactions can be envisaged as liquid-like aggregates which under varied conditions lead formation of lead to formation of multiple polymorphs during in-situ cryo-crystallization.

Topological Effects on Movements of Charged Macromolecules in Crowds

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Abstract:

Charged macromolecules dispersed in aqueous media are ubiquitous since life began on Earth and continue to catalyze formulations of modern materials. Understanding of movements of charged macromolecules in crowded environments remains as a huge challenge due to long-ranged nature of both the topological correlation from connectivity of macromolecules and electrostatic correlation from the charges in the system. Such strongly correlated systems exhibit a variety of rich phenomenology unparalleled in uncharged systems. Recent advances on the dynamics of charged macromolecules in solutions will be presented. In particular, the “ordinary-extraordinary” dynamics, single molecule translocation through a protein channel under coupled forces, and the newly discovered topologically frustrated non-diffusive dynamics of charged macromolecules inside hydrogels will be discussed.

Photoluminescence and Ultrafast Dynamics of All-Inorganic Perovskite Nanocrystals

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Abstract:

Organic-inorganic lead halide perovskite nanocrystals have received great attention in recent years due to their potential applications in low-cost efficient photovoltaic devices.¹ More recently, cesium-based all-inorganic perovskite nanocrystals have also come into prominence through their applications.² However, despite growing interests on these substances, the fundamental photo-induced processes, whose understanding is key to exploitation of these nanocrystals in potential applications, have remained largely unexplored. In this talk, some of our recent studies on ultrafast charge carrier dynamics, fluorescence blinking and photoactivation of cesium lead halide nanocrystals, carried out employing femtosecond time-resolved pump-probe and fluorescence correlation spectroscopy techniques, will be presented.³⁻⁸

References:

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Towards Non-Equilibrium Supramolecular Polymers

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Abstract:

Keywords: Molecular Self-Assembly, Fuel-Driven, Supramolecular Polymerization, Non-equilibrium Self-Assembly

Self-assembly has always been a promising route to achieve novel materials. This has been possible by decades of research and laying down of principles governing the phenomenon. Almost all of this assembly is under thermodynamic parameters and provide minimal help in exploring a temporally driven dimension of self-assembly. On the other hand in biological systems, which have always served as an omnipresent inspiration for self-assembly, control their aggregates and function temporally with unparalleled deft. Considering the conventional self-assembly one wonders if the complexity and dexterity of biological systems is ever to be matched and perhaps one might tread on diverse scientific routes for kinetically controlled self-assembly.

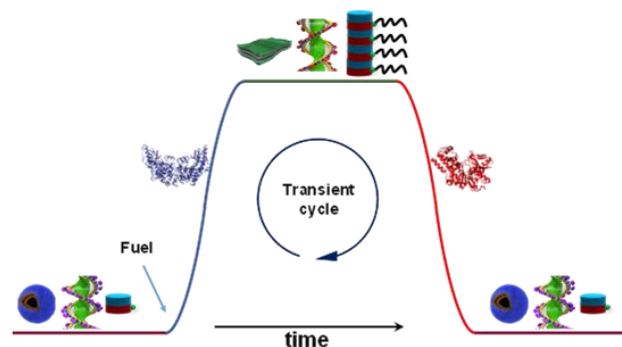


Fig. 1. Fuel-Driven, non-equilibrium supramolecular assemblies in our laboratory.

We, in our laboratory, are driven by this philosophy and are currently trying to understand both thermodynamic and kinetic aspects of self-assembly. This talk describes our efforts in understanding a very key concept of biological self-assembly which is temporal control over aggregates via a chemical fuel as we think this approach can singlehandedly cater to various existing challenges of supramolecular chemistry such as a living supramolecular polymerization, control over nucleation rate, transient materials and formation of supramolecular hetero-structures.

I will be discussing our results by taking supramolecular systems, which we have been working on during the last few years.

References:

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Looking out for Green tea polyphenols

Swagata Dasgupta* and Susmitnarayan Chaudhury

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Abstract

Protein condensation diseases render the study of their inhibition an interesting area of research. For example, amino acid modifications and/or aggregation in human γ -crystallin and other members of the crystallin superfamily are the main causes of cataract formation. *In vivo/in vitro* factors like ultraviolet (UV) radiation, pH, temperature and exposure to chemical agents result in a disruption of the structural integrity of the proteins. The ability of green tea polyphenols in the prevention of angiogenesis and the fibrillation of proteins shows their immense potential. A decrease in the extent of Trp residue oxidation of the cataractous human α -crystallin in the presence of the major green tea polyphenol, (-)-epigallocatechin gallate (EGCG) has been observed. Recombinant human γ B-crystallin overexpressed in *E. coli* exposed to UV radiation under physiologically relevant conditions in absence and presence of different concentrations of green tea polyphenols show their potency against oxidative photodamage of the protein. The low pH and elevated temperature mediated aggregation of recombinant human γ B-crystallin confirms the amyloid like fibrillar nature of the human γ B-crystallin aggregate. It has been observed that disruption of the fibrillar network is possible with green tea polyphenols.

References

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Using operand Raman spectro-electrochemistry to understand support-catalyst-electrolyte interface and interplay in alkaline hydrogen evolution reaction

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Comprehending the mechanistic involvement of support-catalyst interface is critical for effective designing of industrially relevant electrocatalytic processes such as alkaline hydrogen evolution reaction (alHER). The understanding of kinetically sluggish alHER exhibited by both Pt and Pt-group-metal-free catalysts is primarily derived from secondary electrochemical parameters such as Tafel slope. Contributing to this understanding, we employ operando Raman spectroelectrochemical measurements for direct identification of the rate-determining, crucial metal-oxohydroxo intermediates during alHER and thereby provide mechanistic insights for rational design of the support-catalyst interface. Specifically, interfacial nano-engineering of a newly designed carbon support (Gyroid-like carbon nanosphere, GCN) with a spinel Co_3O_4 nanocube catalyst is demonstrated to achieve facile alHER ($-0.46\text{ V @}10\text{ mA/cm}^2$). Such efficient alHER is mainly attributed to the unique lamellar morphology with high mesoporous surface area ($936\text{ m}^2/\text{g}$) of GCN that catalyses the rate-determining water dissociation step and facilitates rapid ion diffusion. The dissociated water participates in the formation of Co-OOH intermediate, as evidenced for the first time through the emergence of $\nu\text{Co-OOH}$ Raman peak (1074 cm^{-1}) under operando conditions. Subsequent alHER proceeds through Volmer-Heyrovsky route (119 mV/dec) via $\text{T}_d\text{ Co}^{2+} \leftrightarrow \text{Co}^{3+} \leftrightarrow \text{Co}^{4+}$ oxidative pathway. Concomitant graphitization of GCN through the disappearance of $\nu\text{sp}^3\text{C-H}$ (2946 cm^{-1}) supports the co-operative dynamics at the Co_3O_4 -GCN interface. Thus, the nanostructured GCN synergistically transforms the conventional OER/ORR-catalyst for active alHER. Furthermore, the low charge-transfer resistance ($R_{\text{ct}}=35.8\ \Omega$) and highest capacitive double layer ($C_{\text{dl}}=410\text{ mF/cm}^2$) achieved among all nanocarbons highlights the effectiveness of GCN, besides providing new parametric descriptors for electrocatalytic processes.

**“De Novo Oligosaccharide Synthesis and Medicinal Chemistry:
Use of the Taylor catalyst in a Pd/B-catalyzed Abiotic Glycosyl-Transferase”**

George A. O'Doherty
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Abstract:

We all possess a never-ending desire to mimic the elegance that exist in nature. This design principle has become a major aspiration in both art and science. For organic chemist this can be seen in the pursuit of the synthesis of natural products, as well as, in the design of new reaction catalysts that mimic enzyme efficiencies. Of all the aspects of enzyme catalyzed reactions to mimic the selectivity of the glycosyltransferase stands as the “Holy Grail” in terms of substrate-, regio- and stereo-selectivity. Recently we have found that the use of the Taylor catalyst ($\text{Ph}_2\text{BO}(\text{CH}_2)_2\text{NH}_2$) as the regioselective activator component in a Pd(0)-catalyzed glycosylation (*i.e.*, pyranone installation) can result in a reaction with glycosyl-transferase like selectivities. A reaction where this dual B/Pd-catalyst system mimics the nucleophilic and electrophilic activation sites of the enzyme. Key to this mimicry is the recognition that pyranone rings can serve as atomlessly protected stable forms of monosaccharides. In this regard, we have been working to develop practical catalytic asymmetric approaches to the synthesis and study of stereochemically complex oligosaccharide structural motifs, using of asymmetric catalysis. This reliance on catalysis for stereocontrol can be seen in the asymmetric synthesis of the key pyranone building blocks from achiral furans, the diastereoselective assembly of these pyranones in to oligomers and finally the regio- and stereoselective bidirectional-functionalization of these oligomers into oligosaccharides. This effort and its application for oligosaccharide synthesis and related medicinal SAR-chemistry studies will be discussed.

Total Synthesis Driven Methodologies

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Abstract:

The structural complexity and skeletal diversity of natural products have served as inspirations to organic chemists for the discovery and design of new synthetic methods en route to their chemical synthesis. Our group focuses on the development of catalytic/methodologies that are specifically designed in the context a total synthesis of natural products of biological relevance. In this presentation, we wish to provide a comprehensive compilation of various catalytic/transformations that have been developed in our group along with some salient aspects of the accomplished total synthesis.

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Molecular Magnets as MultiFerroic Materials

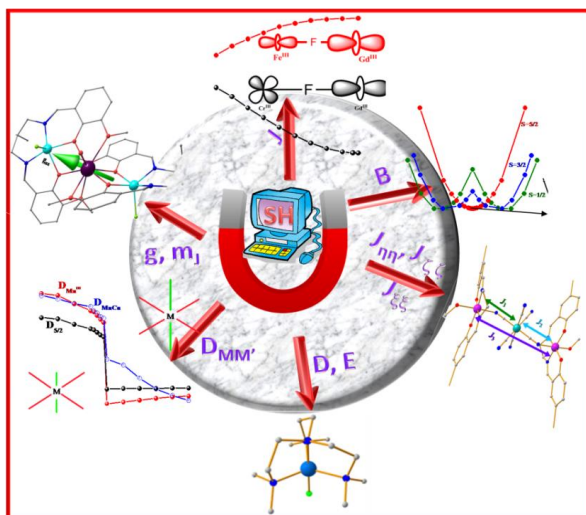
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Abstract:

Molecular magnetism is one of the vastly growing research fields with an aim to design the molecules and materials with tuneable magnetic and electronic properties.^{Error! Reference source not found.} Their synthesis, characterization and implementation as devices which creates lively crossroad among chemistry, physics and material science: a multidisciplinary research field. These molecules have wide spread potential applications ranging from magnetic storage devices, spintronics, Q-bits in quantum computing to magnetic coolants.^{Error! Reference source not found.} Single-molecule magnets (SMMs) are the molecules which show slow relaxation of magnetization below the critical temperature and exhibit hysteresis loop similar to classical magnets. SMMs offer key advantage over classical magnets due to their light weight, solubility and multifunctional behaviour. Theoretical tools are indispensable in this arena² for understanding the observed magnetic properties. The strength of these methods is not only limited rationalization but also to predict novel molecules which can exhibit superior magnetic properties. In this presentation, I will research effort undertaken in our group towards achieving this goal.²



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Transition Metal-Free C-C Coupling Catalysis

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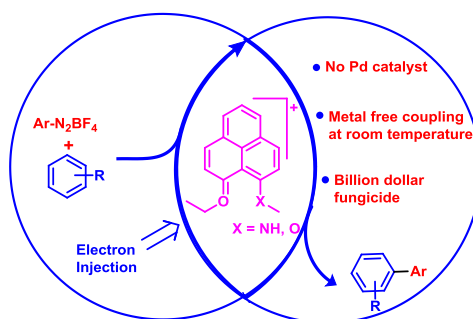
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Abstract:

In 2010, the Nobel prize in Chemistry was awarded for development of Pd-catalyzed C-C coupling which has direct impact in a numerous industrial processes. Today's major concerns on the industrially used catalytic systems have been: i) high expense of catalysts; ii) toxicity of transition metals; iii) difficulties in removal of trace amounts of toxic-metal residues from desired product; and finally iv) the large consumption of heavier and rare transition metals which do not meet the requirement of sustainable development. In this regard, the development of environmentally benign cost-effective catalysts is ideal. Naturally, the most recent trend in catalyst development heralded a new era using either earth-abundant, nontoxic, and inexpensive metals or metal-free catalysis.

This talk will discuss our recent developments on this concept^[1-7] how systematically one can avoid Pd-metal based catalysts to develop C-C coupling catalysis. The emphasis will be given on how we came up with the development of the present concept in catalysis, which was primarily triggered by an entirely different area of spin electronics.^[3, 8]



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Molecules or Molecular assemblies for Predictive Responses.

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Abstract:

Purpose-built molecules that are capable of functioning in a predictive manner in the presence of a certain external stimulation is an important area of contemporary research and has significance for chemistry, clinical biology, diagnostic and photoactive smart material. Various photo-induced responses are being utilized for designing such photoactive molecules. Derivatives of various photoactive molecule with diverse photo-induced responses have been extensively used by researchers active in these areas. Rich photophysical properties, the stability of the photoinduced excited states and reversible redox behavior are crucial parameters that need to be considered while designing a receptor specific for each of these various applications. Our research interests include harnessing both coordinative interactions as well as various nonbonding interactions for realizing our goal. Noninvasive imaging approach is preferred for observing individual events in cells, as imaging studies are performed in physiologically authentic environments and have relevance for cell/molecular biology for studying biochemical processes. There are significant activities in designing appropriate drug carrier or imaging reagent for site specific drug release or visualization of specific organelles in the membrane-enclosed intracellular structures either for improving drug efficacy or gaining insight for monitoring important biological processes. Stability towards photo-bleaching, cell membrane permeability, nominal cytotoxicity and luminescence in the longer wavelength following excitation with non-harmful visible light are some of the essential criteria for any such efficient imaging reagents. Some of our recent efforts in addressing these issues the area of cellular imaging and photo-induced toxicity shall be discussed.

Enantioselective Conjugate Addition Reactions

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Abstract:

Enantioselective conjugate addition reactions (1,4- & 1,6-) are quite important in organic synthesis. 1,4-Conjugate addition involves addition of nucleophiles to a β -carbon of a conjugate system from a particular face.¹ Although a lot of work has been done for this type of reaction using chiral Lewis acids, the system still poses some challenge for reactions using chiral organocatalysts. It is even more challenging to control facial selectivity for addition of nucleophiles to a δ -carbon (1,6-addition), due to distance from the reactive functionality. In this lecture, I will describe our efforts in this direction.^{2,3} I will also talk about asymmetric vinylogous Michael reaction using chiral organocatalysts.⁴

References and Notes:

1. Rout, S.; Ray, S.K.; Singh, V.K. *Org. Biomol. Chem.***2013**, *11*, 4537 and references cited therein.
2. (a) Rana, N.K.; Selvakumar, S.; Singh, V.K. *J. Org. Chem.***2010**, *75*, 2089. (b) Rana, N.K.; Singh, V.K. *Org. Lett.***2011**, *13*, 6520. (c) Molleti, N.; Rana, N.K.; Singh, V.K. *Org. Lett.***2012**, *14*, 4322.
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Computations Experiments
Challenges in Synergizing Asymmetric Catalysis

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Abstract

Computational quantum chemistry has been increasingly employed toward rationalizing the stereochemical outcome in catalytic reactions.¹ In our laboratory, ab initio as well as DFT methods are employed to gain insights into carbon-carbon and carbon-heteroatom bond-forming reactions of immediate practical significance.² The key objective of our research is to gain molecular insights on the factors responsible for stereoselectivity and to exploit such insights toward *in silico* design of novel asymmetric catalysts.³

Through this talk, we intend to propose the need for a timely rethink on a number of working hypotheses on asymmetric induction that places an over-emphasis on steric interaction. In general, the presentation would encompass a few contemporary themes in the domain of asymmetric multi-catalytic reactions.⁴ Interesting interpretations/rationalizations of experimental observations besides meaningful guidelines for rational improvements in the design of asymmetric catalysts would remain the key focus of the presentation. The contents are designed to cater to a broad and diverse group of audience; hence, the chemical insights would be emphasized, rather than a labyrinth of technical details.

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1. (a) Sunoj, R. B. *Wiley Interdisciplinary Reviews: Comput. Mol. Sci.* **2011**, *1*, 920. (b) Sunoj, R. B. *Acc. Chem. Res.* **2016**, *49*, 1019.
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Exocyclic olefinic maleimides as versatile scaffolds for bioconjugation.

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Abstract:

The development of chemoselective organic reactions that proceed rapidly under physiological conditions to form stable covalent linkages with biomolecules have revolutionized modern biological and clinical research. One such reaction, Michael addition between the thiol functional groups of cysteine residues of proteins and maleimides to form thio-maleimide linkages, is extensively used for labeling proteins with fluorophores, affinity tags, polyethylene glycol moieties and drug molecules for a diverse range of applications. In particular, the tremendous success of antibody-drug conjugates (ADCs) generated by appending drug molecules to antibodies by employing this chemistry has had a transformative impact on cancer therapy. Consequently, recent reports on the susceptibility of these linkages to undergo thiol exchange-mediated breakdown in the physiological milieu are extremely alarming^{1,2}. In this talk, I will present our recent work that unlike conventional maleimides, exocyclic olefinic maleimides form thiol exchange-resistant conjugates and hence are preferable for thiol bioconjugation³. I will also discuss our new strategy of installing exocyclic olefinic maleimide at the *N*-terminus of proteins and employing it for generating a diverse variety of dually labeled protein bioconjugates⁴.

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Indoleamine-2,3-dioxygenase (IDO) Inhibition as a strategy to Augment Cancer Immunotherapy

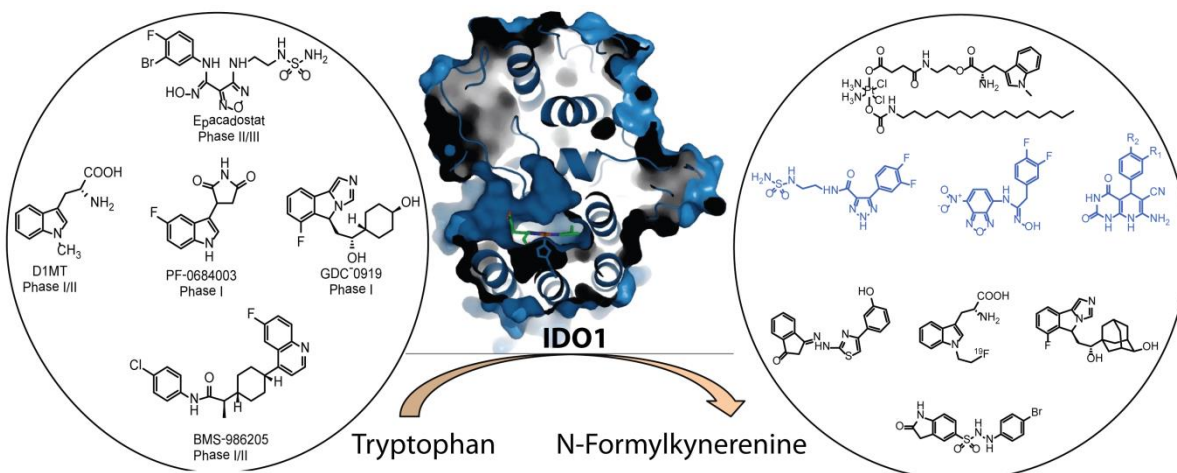
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Abstract:

Immunotherapy is presently considered as one of the most promising approaches in the battle against cancer. Recent accomplishment with the immune checkpoint inhibitors against a wide range of cancers has made cancer immunotherapy as one of the most exciting developments. Early data from human trials—suggest one way to boost the activity of checkpoint inhibitors is to also target indoleamine 2,3-dioxygenase (IDO1) enzyme. A rising number of small-molecule based IDO1 inhibitors are in or poised to enter the clinic trials. With the aim of discovering novel IDO1 inhibitors, we have synthesized oxindoles, *N'*-hydroxyamidines, 1*H*-indazoles, dipyrazolopyrans, 1*H*-pyrazoles, 1,2,3-triazoles and others. Few of these heterocyclic compounds are endowed with an inhibitory potency in the nanomolar range. Through this talk, I will discuss about the detailed synthetic strategy, inhibitory activities, enzyme kinetics, biological activates and Structure-Activity-Relationships (SARs) of these compounds.



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Singlet Exciton Fission in Conjugated Organic Molecules

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Abstract

Over the past decade, organic photovoltaics have emerged as a competing technology to Silicon-based solar cells due to lower processing cost, and the large chemical space available to the choice of the photoactive material. With efficiencies reaching >12%, the community is currently looking forward to new ideas for making devices which can compete with the other alternate technology of inorganicorganic hybrid perovskites. In our group, we have been interested in understanding the exciton dynamics in variety of conjugated polymers [1, 2] that forms the material basis for organic solar cells. In certain classes of organic chromophores, Singlet excitons can dissociate into energy conserved Triplet excitation pair thereby creating two photoexcited molecular entities per photon. This photophysical process is called Singlet Fission, and has been of enormous interest since its first report. [3] I will describe the recent time-resolved experiments in our lab which has helped identify mechanisms of singlet fission in three classes of chromophores: carotenoids, diketopyrrolopyrroles [4] and pentacenes [5]. We find that for all these chromophores, optimal packing leads to generation of triplets in 10s to 100 of picoseconds.

References:

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Single Molecule Switching and Sensing

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Abstract:

Charge transport through and between molecules is central to important processes in nature. Studying the conductivity of single molecules can contribute to a better understanding of charge transport, and also help develop building blocks of molecular electronics, light harvesting devices, etc. We measure the conductivity of molecules using the Scanning Tunneling Microscope break-junction (STM-BJ) method that utilizes repeatedly formed circuits where one or a few molecules are trapped between two electrodes, at least one of which has nanoscale dimensions. The statistical analysis of thousands of measurements yields the conductance of single molecules.

One particular interest is the role of the molecule-electrode contact in charge transport. In the simplest analysis this contact can present a substantial barrier to charge injection, which can have important consequences in devices such as dye sensitized semiconductor nanoparticle solar cells. We have demonstrated that carbodithioate termination of molecules can enhance conductivity by an order of magnitude.[1] We have also shown how the sensitivity of the electrical conductivity of single molecules to external perturbations can allow for switching and sensing,[2] as well as the use of single molecule conductance for the discovery of novel materials.[3] Our most recent developments include controlling the orientation of the molecule in the junction so that we can measure conductance along different molecular axes, accessing elements of the anisotropy of the single molecule conductance tensor.

References:

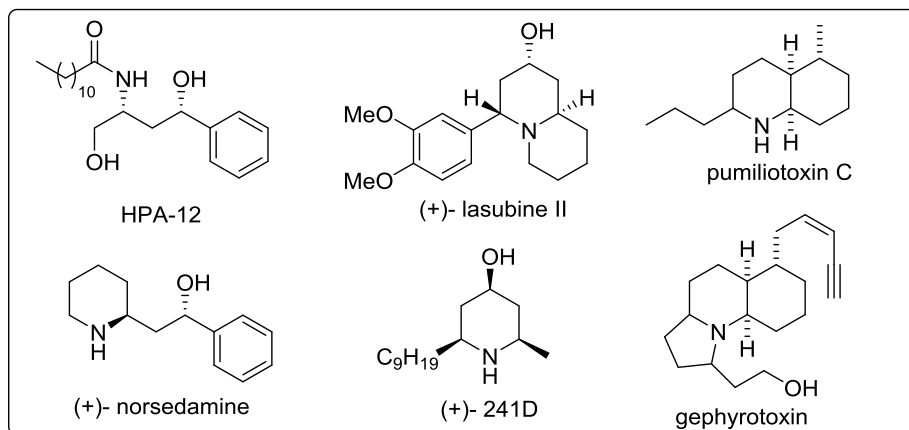
1. Regulating a Benzodifuran Single Molecule Field Effect Transistor via Electrochemical Gating and Optimization of Molecule/Electrode Coupling, Zhihai Li, Hui Li, Songjie Chen, Toni Froehlich, Chenyi Yi, Christian Schönenberger, Michel Calame, Silvio Decurtins, Shi-Xia Liu, and Eric Borguet, *Journal of the American Chemical Society* 136 (25), 8867–8870 (2014)
2. Single-Molecule Sensing of Environmental pH-an STM Break Junction and NEGF-DFT Approach, Zhihai Li, Manuel Smeu, Sepideh A. Mamaghani, Yangjun Xing, Mark A. Ratner and Eric Borguet, *Angewandte Chemie*, 126 (4), 1116-1120 (2014)
3. Towards Graphyne Molecular Electronics, Zhihai Li, Manuel Smeu, Arnaud Rives, Valerie Maraval, Remi Chauvin, Mark A. Ratner, and Eric Borguet, *Nature Communications* 6:6321 (2015)

Diverted Total Synthesis: From Macrolactones to Alkaloids

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Abstract:

Our research group has been involved in the total synthesis of polyketide natural products using chiral pool tartaric acid and chiral furyl carbinols as the four carbon four hydroxy synthon. During the course of our synthesis of the natural product schulziene B, we had an unexpected entry to the realm of sulfinimine chemistry. This led to us to develop procedures for the direct addition of ketones, substituted methyl enones and other nucleophiles to non-racemic sulfinimines. In this talk, these addition reactions and their application to the total synthesis of alkaloids will be discussed.¹⁻⁴



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Development of New Synthetic Strategies and Tactics: Their Impact, Implications, and Applications

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Abstract:

In this lecture, I will discuss various methodologies developed in our group to design a wide variety of polycycles. In this regard, we have used ronalite chemistry, metathesis, cross-couplings, and [2+2+2]-cyclootrimerization as key steps. Additionally, we will cover impact and applications of these methods. By utilizing these methods, we have synthesized star-shaped molecules, conformationally constrained α -amino acid derivatives, and heterocycles.

References and Notes:

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Propargylic Alcohols in Annulation Reactions: Recent Endeavors

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Abstract:

Over the decades, significant progress is being made in several key research areas, such as catalysis, the design of safer starting materials, environmentally benign solvents and the development of renewable feedstock's. The design of starting materials that produce the environmentally benign by-products has been one of the most active areas. Towards this, propargylic alcohols have attracted wide attention and their conversion in to the desired polycyclic aromatic hydrocarbons (PAHs) and heterocycles through the annulations. Besides, the ease of preparation and availability also makes propargylic alcohols as attractive precursors. The present lecture will highlight the recent accomplishments with regard to development of annulation reactions involving propargylic alcohols towards the aromatic and heteroaromatic molecules, including few natural products.¹⁻⁸

References:

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Reactivity of Main-Group Compounds Containing Double Bonds

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Abstract

Multiple bonds between heavier main-group elements although known for some time now continue to be of topical interest both from the point of view of synthetic chemistry as well theoretical chemistry. One of the general strategies to assemble such compounds is to utilize sterically encumbered substituents on the main-group elements. We describe strategies that have allowed us to prepare and fully characterize new hetero-element compounds that contain Si=N and Si=P bonds. An interesting aspect of these compounds is the presence of potentially reactive Si-H bond. These compounds were prepared by a direct synthetic route involving dehydrohalogenation across a Si-N/Si-P bond from Si(IV) precursors. The Si=N analogue shows an interesting addition of H₂O across the multiple bond. We also describe activation of a P=P bond towards reactivity with water or BH₃·NH₃. The activation of the otherwise sluggish P=P bond was accomplished by reaction with N-heterocyclic carbenes (NHCs) which affords a reversible binding (Figure) .³ Finally, some interesting reactivity of NHCs and cyclic(alkyl)(amino)carbenes(CAACs) is described.

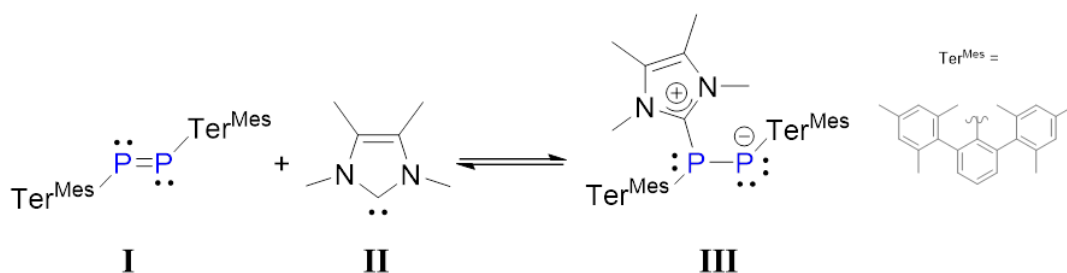


Figure: The reversible binding of NHC^{Me4} to a compound containing the P=P bond

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Redox-Active Mesoionic Carbenes for Redox-Switchable Catalysis

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Abstract:

Mesoionic carbenes (MICs) of the 1,2,3-triazol-5-ylidene type are promising ligands in organometallic chemistry and homogeneous catalysis.¹ While the modular synthetic route to these classes of ligands make their steric tuning rather straightforward, very little is known regarding the electronic tunability of these MICs. In this contribution we will report on recent strategies developed in our laboratories towards switchable tuning of the electronic properties of MICs. In doing so, we will report on (di)cationic MICs, a class of ligands that were unprecedented before the recent reports from our group.^{2a,b} Redox and IR-spectroscopic results on Ir-CO complexes of these redox-active MICs will be reported to determine their Tolman Electronic Parameters. We will then report on Au(I)-complexes with the redox-active MICs and show the first examples of redox-switchable Au(I)-catalysts (Figure 1).^{2c,d} The results in this contribution will thus display redox-active MICs as potent ligands in redox-switchable catalysis.

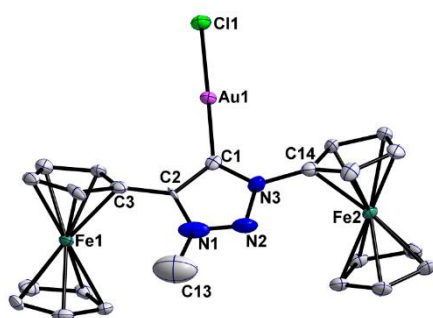


Figure 1. A gold(I) complex with a redox-active mesoionic carbene

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Structural modification in reverse micelles and growth of anisotropic nanostructures

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Abstract:

One of the crucial factors in implementation of nanomaterials for fabrication of devices with desired function is precise control of their dimensions. Novel applications of these materials are attainable due to extraordinary chemical and physical properties governed by their shape and size. Designing nanostructures of desired morphology using microemulsions(1,2) require development of new synthetic protocols to stimulate structural alterations in templates, modulating the architecture of nano-metric structures. We have developed structural modifications in a tunable soft template(reverse micelles) and investigated the growth of nanostructures within these nanotemplates. Using various techniques like time-resolved spectroscopy, SAXS, FCS, and ^1H NMR studies we aim to understand the effect of surfactant, co-surfactant, hydrotrope (sodium salicylate) concentration and water-to-surfactant molar ratio (W_x) on the shape, size, intermicellar interaction and other structural parameters in CTAB or CPB/butanol/water/isooctane reverse micellar system(3-7). We further investigated the growth of phosphor nanoparticles with in reverse micellar system using time-dependent SAXS measurements to understand morphological evolution of these materials. We have also explored the temporal evolution of anisotropic nanostructures by the solvation approach using time-resolved studies(8) of nanorod and nanocube of different systems (iron oxalate follows slow kinetics and zinc oxalate and copper oxalate both follow fast kinetics) in quaternary reverse micelles. The obtained solvation reorientational dynamics profile qualitatively the distinct stages in the heterogeneous evolution of the anisotropic nanostructures which have implications in developing new synthetic protocols for potential anisotropic nanostructures.

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Photoprotection pathways in human skin pigment eumelanin

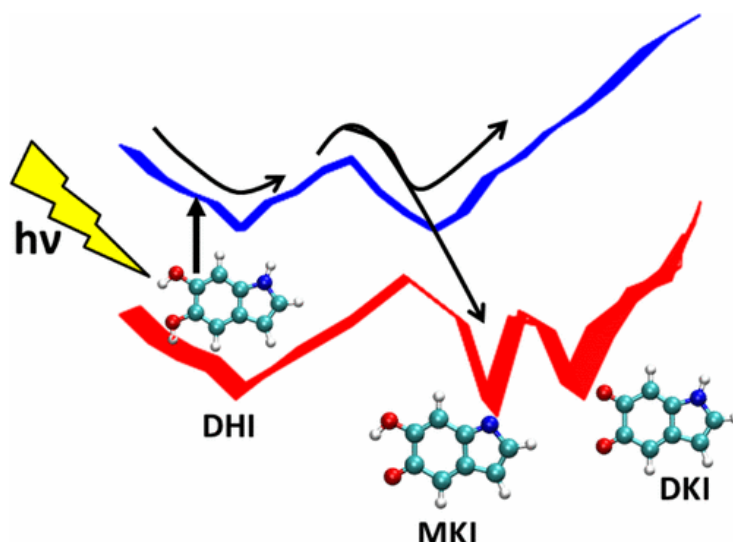
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Abstract

Eumelanin, the functional polymer in human skin, forms a heterogeneous layered structure intrinsic to its broadband monotonic spectra. The inherent structural heterogeneity of eumelanin makes the photoprocesses very complex and diverse in nature. Due to this diversity, a complete mechanistic picture of these photoprocesses, essential to understanding the photoprotective properties, has been missing to date. We recreate the potential energy surfaces of the low-lying excited states of the multiple monomeric forms of eumelanin constituents that play a prominent role in either photoprotection or photodamage pathways. Our results indicate a diverse set of pathways for the photoexcited species to relax back to the ground state, that depends on the specific monomeric form. Furthermore, the excited state reaction channels show the scope of extensive interconversion between the different monomers and therefore, we propose that the heterogeneity of eumelanin is key to its photoprotection capability.



Hybrid Quantum-Classical Studies of an Enzymatic Reaction in Aqueous Medium

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Abstract

We will discuss our recent studies of transamination reaction in aqueous medium. Transamination constitutes an essential step in many biological processes catalyzed by pyridoxal 5'-phosphate (PLP) dependent enzymes [1-3]. It involves conversion of an internal aldimine involving PLP and the enzyme to an external aldimine involving PLP and the substrate amino acid [4]. We have explored the mechanism and free energetics of transamination process at the active site of serine hydroxymethyltransferase (SHMT) [5] and looked at the involvement of various active site residues in the process by means of hybrid quantum-classical simulations combined with enhanced sampling techniques.

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Targeting structure specific DNAs and Proteins for therapeutic and sensor applications

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Abstract

The research on the structural diversity of biomolecules, especially that originate from DNAs and Proteins, has received much attention in recent years and numerous reports appeared probing its detection, structure, stability, reactivity, selectivity, etc. In other words, they are the prospective targets for chemical intervention of biological functions for therapeutics and sensor applications. Targeting the activity of these intriguing functional templates through noncovalently interacting guests poses challenges to identify such structure specific ligands, which can discriminate it from other forms and report its presence optically. This presentation will provide an account of our recent activities, on the intriguing fluorescence properties showcased by certain fluorogenic materials on its binding to the G-quadruplex DNAs and protein assemblies/fibrils. Our studies on human telomeric G-Quadruplex DNA opened up avenues to explore highly specific quadruplex sensing agents for diagnostic, therapeutic and cation sensing applications [1]. Aptly, these selective and sensitive emission features have been turned into label-free fluorescence-based detection of various metal ions and small biomolecules, down to pico molar range, having promising bio-analytical applications [2]. On the other hand, one of the most striking characteristics of proteins, specifically, that of insulin, is its ability to form different association states including dimers, tetramers and hexamers. Also its aggregation into insoluble amyloid fibrils and plaques remained an intriguing phenomenon and is a hot topic of contemporary research. In a recent attempt we have demonstrated an efficient formation of a hexameric assembly by human insulin protein promoted by a structure specific TPM dye, Ethyl Violet, especially in the absence of any metal ions [3]. These assemblies have been further established to be potential for developing long acting insulin formulations, drug delivery applications and as photo-therapeutics. With regard to the fibril formation, we contributed by demonstrating the evaluation of fluorescence lifetime of an extrinsically added fluorogenic dye, as the more sensitive and convenient method for the assessment of fibrillation in the pre-fibrillar regime. Developing methods/materials for intervention/inhibition of fibrillation is one of the therapeutic approaches to avoid the fibril-associated amyloidosis and neuro-degenerative diseases [4]. The presentation will cover details of these studies and their future perspectives.

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The Tale of Two Tetretylenes for Cu(I)- and Au(I)-Arene Complexes

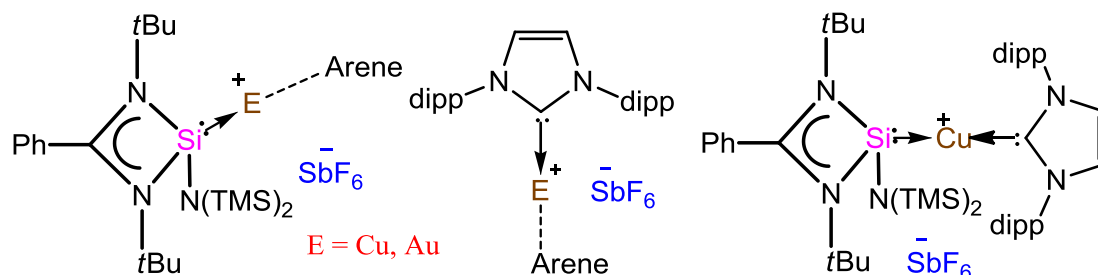
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Abstract:

The interaction of transition metals, especially the coinage metals (Cu, Ag, Au) with arenes is of high importance as they serve as the key intermediates in various catalytic reactions e.g. cycloaddition, cross coupling, cycloisomerization, C-H functionalization and also display multifarious coordination chemistry. However, the isolation of these complexes is a challenging task due to weaker interactions between them. We have explored the utility of silylene, $[\text{PhC}(\text{NtBu})_2\text{SiN}(\text{SiMe}_3)_2]$, as a ligand to prepare the Cu(I) and Au(I)-arene cationic complexes.¹ An appealing facet of $[\text{PhC}(\text{NtBu})_2\text{SiN}(\text{SiMe}_3)_2]$ is that it accepts electron density from the metal as evidenced in its coinage metal complexes.² This potential has been duly realized through the isolation and characterization of an unprecedented $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$ and $[\text{Au}(\eta^1\text{-C}_6\text{H}_6)]^+$ complexes.^{3,4} For a direct systematic comparison, we have carried out the same reactions with *N*-heterocyclic carbene which reveals, unlike silylene, there is no $\text{M} \rightarrow \text{C}_{\text{NHC}}$ back-bonding. These complexes are further used for their reactivity study and catalytic application.



Arene = benzene, hexamethyl benzene, toluene, xylene

Chart 1. Selected Si(II) supported Cu(I) and Au(I)-arene complexes.

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Investigation of Novel Nano-structures for the Methanol Oxidation Reaction

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Abstract

Over decades, direct methanol fuel cells (DMFCs) have received considerable attention among energy harvesting systems due to the unique possibility of direct conversion of fuel (methanol) into the electricity. Even though, lot of non-platinum based composite materials have been tried, Pt based catalyst are still prevailing in DMFCs due to faster oxidation of methanol on Pt. However, inherent tendency of Pt to get poisoned by adsorbed CO is holding back its commercial production in a bigger way. One way to surmount this challenge is to choose a novel supports/co-catalysts which will continuously provide hydroxyl groups for the oxidation reaction and will reduce the impact of poisoning. Furthermore, little attention has been given to develop specific electroanalytical methodology to probe CO adsorption reaction in a real time.

With this motivation, electro-catalytic oxidation of methanol on Pt nanoparticles loaded silica hollow spheres based electrodes was investigated in details. In spite of the poor conducting nature of the silica support, the oxidation potential and current density per unit mass for methanol oxidation were improved, substantially. This outstanding performance is attributed to the facile reaction between adsorbed CO on Pt with a surface hydroxyl groups present on hollow silica.

To monitor CO adsorption on electro-catalyst during methanol oxidation, novel fast scan cyclic voltammetry (FSCV) based method has been developed. To perform cyclic voltammetry measurements at higher scan rates ($\sim 10^4$ - 10^5 mV s⁻¹), Ultra-micro electrode (UME) geometries loaded with the catalysts has been employed. Peaks associated to CO adsorption have been elucidated as a function of scan rates. From that data, the average rate of CO adsorption in methanol oxidation has been quantified. This method can be generalize to any electro-catalysts of interest.

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Emergence of Chiral Structures in Lyotropic Liquid Crystals

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Abstract

Crystallization of tartrates by Pasteur provided the first glimpse of spontaneous mirror-symmetry breaking, and that led to the foundation of stereochemistry as a discipline. A consequence of mirror-symmetry breaking is optical activity, and since the time of its discovery by Biot in the early 1800s, has fascinated scientist. Since those early studies, the appearance of macroscopic chirality from both chiral and achiral molecules has been on interest. In this talk, we discuss the appearance of macroscopic chiral structures from a class of liquid crystals, referred to as lyotropic liquid crystals, under various conditions.

Synthesis of Biopolymer Mimics via Topochemical Reactions

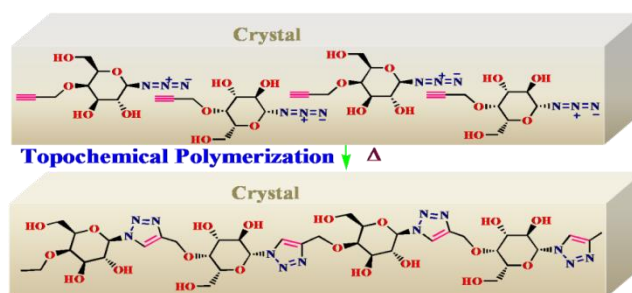
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Abstract

Topochemical reactions, the reaction between pre-organized reacting motifs in the crystal lattice, are attractive as they do not require solvents, catalysts and other special reaction conditions for the reaction and provide products in pure form. Also such reactions provide basic understanding about mechanistic and geometrical details about a reaction.¹ We have employed thermal Topochemical Azide–Alkyne Cycloaddition (TAAC) reaction and light induced topochemical polymerization of diacetylenes to polydiacetylenes (PDA) to synthesize various biopolymer mimics. We have exploited hydrogen bonding for the self-assembly of monomers in solid or gel to pre-organize the reacting motifs. Lattice controlled polymerization/oligomerization reaction of such self-assembled (pre-organized) monomers gave various biopolymer mimics. By applying this methodology, we have topochemically synthesized monodisperse glycopolymers,^{2,3} oligosaccharide mimics,⁴ DNA analogs^{5,6} and polypeptides.⁷⁻¹² Also we have exploited light-induced topochemical polymerization of diynes to polydiacetylenes for various applications.¹³⁻¹⁴ In this talk, the design and execution of such topochemical syntheses and their possible applications will be discussed.



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Metal-Free Approaches for the Construction of Privileged Scaffolds

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Abstract

Heterocycles are common structural motifs present in over 80% of the currently marketed small-molecule drugs in market. Artificially mimicking the heteroatom containing biological molecules such as nucleic acids, amino acids, carbohydrates, vitamins and alkaloids in a subtle manner can lead to potential new drug candidates. Our lab has been actively involved in developing new synthetic strategies to access diverse classes of privileged heterocyclic scaffolds starting from readily available starting compounds. I am going to briefly talk about (i) an organocatalytic intramolecular Morita-Baylis-Hillman reaction,¹ (ii) an unusual organocatalytic γ [C(sp³)-H] functionalization of ynones,² (iii) phosphine-catalyzed intramolecular hydroacylation of ynones,³ and related findings.⁴

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Chemical toolbox for precision engineering of proteins

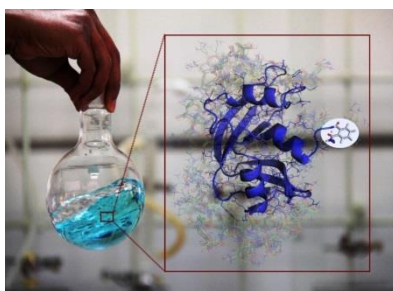
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Abstract:

Chemical biology research often requires precise covalent attachment of tags to the proteins. Such methods enable bioimaging, biophysical investigations, disease diagnosis, and protein-based therapeutics. In this perspective, we have been investing efforts to address three questions. (a) How does the protein behave as a substrate in a chemical transformation? (b) Can we develop chemical methods for single-site modification of native proteins? (c) Is it possible to have a modular chemical method for precision engineering of proteins? The first step toward these targets involves understanding the reactivity landscape of proteins. The critical challenge relates to the identification of physical organic chemistry principles that would allow us to generate reactivity biases at specific sites of the protein. In this perspective, we have developed methods for (a) targeting N-terminus as a reactivity hotspot,¹ (b) labelling the most reactive Lys or His residues,² (c) N-Gly residue specific labelling,³ and (d) modular linchpin directed modification for labeling single His or Lys residue.⁴ These technologies deliver *single-site* installation of various probes in native proteins. The user-friendly protocols result in *analytically pure* labeled proteins. The structure, enzymatic activity, binding to receptors, and downstream signaling pathways are typically unaffected. Also, these technologies allow access to homogeneous antibody-drug conjugates for directed cancer chemotherapeutics.



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Hydrophobic-Hydrophilic interactions in protein folding, protein-protein association and molecular recognition

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Abstract:

Many biochemical processes such as protein folding or self assembly of proteins are highly specific. Proteins fold spontaneously into a very specific 3-dimensional structure. Proteins also associate spontaneously to form multi-subunit macromolecules. These processes occur in aqueous media. The question we pose is what is the role of water in these processes?

Until recently it was believed that the hydrophobic effect, i.e. the tendency of hydrophobic groups to “escape” from the aqueous environment is the dominant driving force for these processes.¹

Analysis of all the solvent induced contributions to the thermodynamic driving forces for protein folding and protein-protein association reveals that, contrary to the commonly accepted paradigm, hydrophilic interactions might be more important than hydrophobic interactions.²

This conclusion was reached after critically examining the data on the various contributions to the driving forces for protein folding, and protein-protein association. Examples on the role of hydrophilic interactions on solubility of proteins, protein folding, protein-protein association and molecular recognition will be presented. Thus, hydrophilic interactions not only helps in understanding the role of water in biochemical processes, but they can also be applies to design drugs that bind stronger to their targets.^{3,4}

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H-bonding Regulated Supramolecular Nanostructures and Impact on Multivalent Binding with Biological Targets

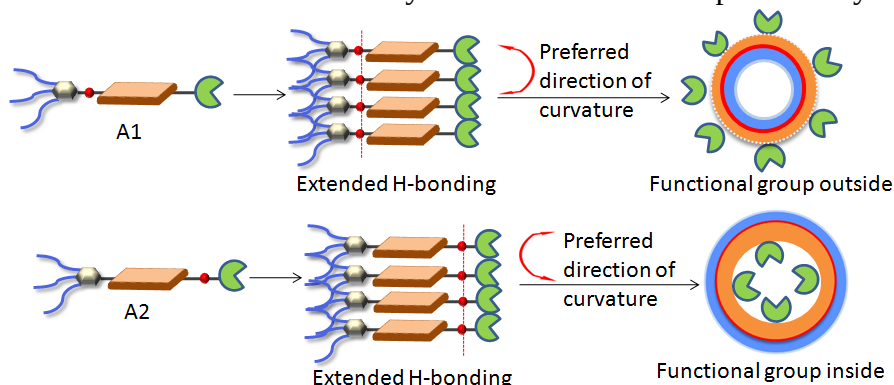
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Abstract

It remains a challenging task to control the functional group display at the inner or outer surface of a vesicle at will. Even though it has been attempted using unsymmetric bolaamphiphiles, lack of control in their lateral orientation results in random distribution of the two different hydrophilic head groups in the exo- and endo- wall. We have recently solved this classical problem by H-bonding functional group attached π -



Amphiphiles (Scheme 1). Basically, driven by the motivation to form extended H-bonding, both A-1 and A-2 undergo uni-directional orientation and furthermore the propensity of the H-bonded chain to remain at the inner wall implicates display of the functional group attached to the H-bonded arm to converge at the inner wall while the functional group attached with the other arm are

displayed at the outer surface. This has been tested with series of unsymmetric bolaamphiphiles having different anionic head groups. Subsequent studies demonstrate the possibilities of precisely tuning the size and surface charge density of such vesicles by systematic variation of the structure of the ionic head groups which was reflected in their ability to inhibit the enzymatic activity of ChT. Most recently, H-bonding regulated functional group display has also been verified by the glycol-cluster effect exhibited by sugar-functionalized similar π -amphiphiles. Hydrazide containing bolaamphiphile produces unsymmetric membrane leading to effective display of the sugar moieties at the vesicular surface which enables much efficient binding with ConA compared to control molecule lacking any H-bonding group. Interestingly when the hydrazide group was replaced by amide, the amphiphile revealed cylindrical micellar structure which appears to endow even better multivalent effect for interaction with biological targets owing to more adaptable nature of cylindrical structure than vesicle. Highlights of these results will be described in the presentation.

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Continuous Flow Materials and Chemicals Manufacturing: A New Paradigm in Process Intensification

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Abstract

Continuous flow manufacturing provides a potential alternative to batch manufacturing because of its inherent advantages such as very efficient heat exchange, high batch to batch reproducibility, fast mixing, high throughput, safety, and the ability to do multistep telescopic synthesis. Due to these advantages, these processes have been referred to as the most promising “Green Technology”. In fact, continuous flow processes are projected to be the “CHEMICAL FACTORIES” of tomorrow. Continuous flow processes also provide “On-Demand” synthesis with complete control over reproducibility, size, shape and these parameters can be achieved at various scales (lab synthesis to pilot to bulk production) with excellent reproducibility. This opens up the opportunity for synthetic chemists to prepare materials with precise control over critical molecular design parameters. It also enables one to carry out chemical synthesis at higher temperatures which were outside the domain of an organic synthetic lab. Apart from this, continuous manufacturing opens up new domains in formulations and various downstream processes. It is also revolutionizing the domain of high throughput machine-assisted synthesis leading to development of Artificial Intelligence (AI) in various domains of chemical industries. In this presentation, I will review some of the recent advances in these directions and some results from our laboratory. An introductory tutorial (developed by us) can be found at YOUTUBE at following address:

<https://www.youtube.com/watch?v=CYo85cdhEfc&feature=youtu.be>

Allosteric Regulation of Transient Molecular Tunnels

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Molecular tunnels in enzyme systems possess variable architecture and are therefore difficult to predict. In this work, we use a combination of computational and experimental approach to resolve the allosteric mechanism as well as pathway followed by ammonia by employing the bi-functional enzyme formylglycinamide ribonucleotide amidotransferase (FGARAT) as a model system. Though its crystal structure has been determined, an ammonia pathway connecting the glutaminase domain to the 30 Å distal FGAR/ATP binding site and the mechanism of cross-talk remained elusive. Crystallography suggested two purported paths: an N-terminal adjacent path (Path1), and an auxiliary ADP-adjacent path (Path2). By using RISM theory which, enables fast and accurate determination of solvent distribution inside protein channel, Path2 was determined as the preferred mode of ammonia transfer. Supporting crystallographic and biochemical studies validate the identity of the path and results lead to the conclusion that the residues in the middle of the channel do not partake in catalytic coupling and serve only as channel walls facilitating ammonia transfer. On the contrary, the regions proximal to the glutaminase active site, where ammonia is produced and those where it is consumed, the end of the channel, are highly sensitive to perturbations. Further to understand how these molecular tunnels are formed atomistic MD simulations in conjunction with experiments were undertaken. Results show that the dynamic catalytic loop, shielding FGAR/ATP has a profound effect on the distal glutaminase activity. Therefore, it appears there exists a relay mechanism triggered by the conformational changes in the FGAR catalytic loop that transmits information pertaining to the progress of the reaction from one active site to another via the N-terminal bridging domain that orchestrates channel formation.

Liquids, Crystals, Liquid Crystals, Plastic Crystals, and More ...

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Abstract

My talk will review the states of matter accessible to condensed phase systems. Atomic solids typically exhibit three phases: long-range center-of-mass order (conventional solid) plus disordered liquid or glass phases. Molecular systems, on the other hand, have orientational (and internal) degrees of freedom, which introduce additional possibilities, even for diatomic molecules, e.g., nitrogen, oxygen and chlorine. Macromolecules with internal degrees of freedom and/or flexibility, such as, surfactants, lipids, dendrimers, etc., self-assemble into an array of distinct condensed phases. Using selective examples, the talk will survey some of the intriguing phases exhibited by Nature.

Abstracts of Poster Presenters

P-1

Synthetic Approach to ABCD ring system of Anticancer Agent Fredericamycin A via Claisen rearrangement and Ring-Closing Metathesis as key steps

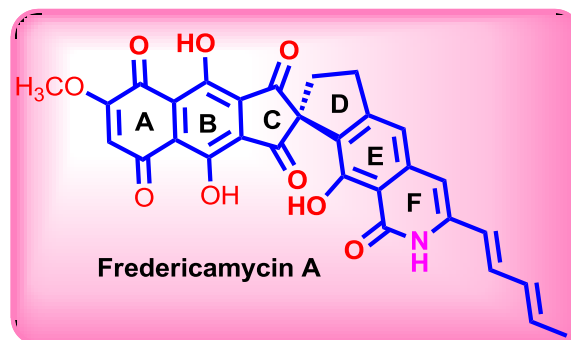
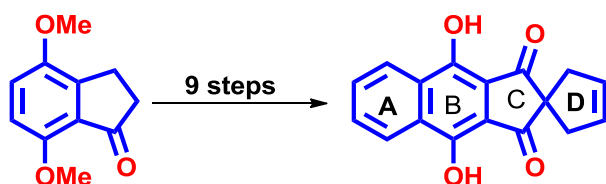
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Abstract:

A new synthetic strategy to ABCD ring system of the antitumor agent, fredericamycin A (NSC-305263) has been realized by Diels–Alder reaction and olefin metathesis as key steps. The tactics developed here for the construction of ABCD ring system also involve double Claisen rearrangement followed by retro-Diels–Alder reaction and two fold ring-closing metathesis. Ring-closing metathesis plays a crucial role in the construction of A and D rings of ABCD core unit. More importantly ABCD fragment synthesis was accomplished without involvement of protecting groups usage.



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P-2

Synthesis and Properties of Benziporphyrinoids

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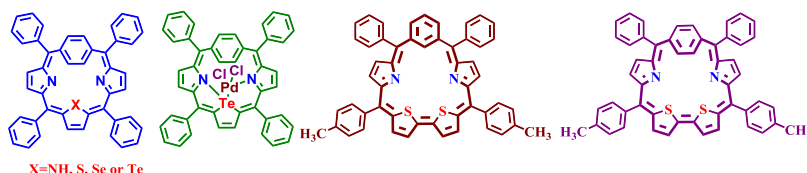
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Abstract:

Benziporphyrins are a class of core-modified porphyrins in which one or two five membered heterocycle(s) are replaced by benzene ring(s). The benziporphyrins are known to show interesting spectral, electrochemical and coordination properties. Specially, the benziporphyrins have high tendency to form organometallic complexes which is the most attractive feature of benziporphyrins. Due to their different properties compared to regular porphyrins, the benziporphyrins are being used in various high technological applications such as MRI contrasting agents, nonlinear optical materials, etc. The next higher homologue of benziporphyrin is benzisapphyrin in which one benzene ring and four 5-membered heterocyclic rings are connected via four *meso* carbons and one direct bond. Regular azasapphyrins are most widely studied expanded porphyrinoids and known for their use as photosensitizers in photodynamic therapy and viral photoeradication^[1]. Heterobenziporphyrins are class of core modified benziporphyrins which are resulted from replacing one or two pyrroles in benziporphyrins with other five-membered heterocycles such as thiophene, furan, selenophene, tellurophene. The heterobenziporphyrins exhibits significant differences in their physicochemical and coordination properties compared to regular benziporphyrins. The perusal of literature revealed that the reports on the heterobenziporphyrinoids are very scarce^[2].

In this context, we have synthesized a series of novel aromatic heterobenziporphyrins by using mild reaction conditions. The compounds were characterized by various spectral and electrochemical techniques, and X-ray crystallography. The coordination properties of the heterobenziporphyrins were explored and shown that only tellurabenziporphyrin forms Pd(II) complex readily. Furthermore, a series of [24 π] nonaromatic dithia *meta*-benzisapphyrins and [22 π] aromatic dithia *para*-benzisapphyrins were synthesized over sequence of steps. The structural, spectral and electrochemical characteristics including aromaticity of the *m*-benzisapphyrins and *p*-benzisapphyrins were discussed with the help of spectra, electrochemical and DFT studies^[2].



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P-3

Design and synthesis of novel polycyclic cage molecules

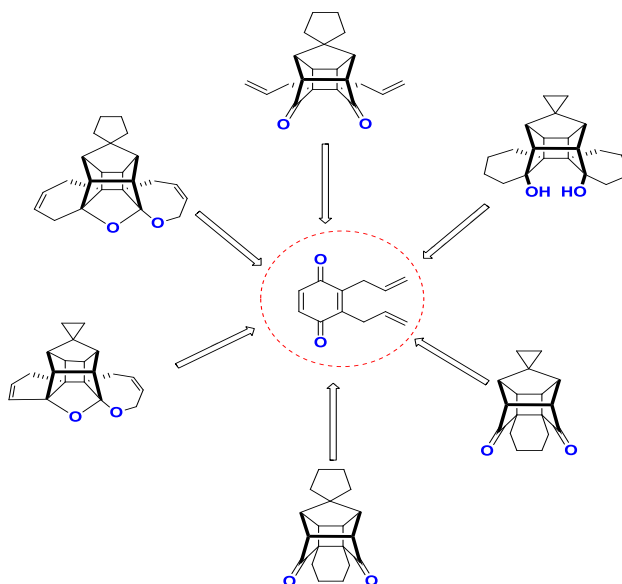
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Abstract:

During the past few decades, polycyclic cage molecules attracted considerable attention of synthetic community due to their useful applications in various fields.^{1,2} These molecules serve as key synthons for various natural product and non-natural product synthesis. Some of these are used as medicinally and pharmaceutical important molecules. In addition, they are also used in supramolecular chemistry as templates for complexation of various metal ions.



Here, we designed various intricate cage systems by using Diels–Alder chemistry and ring-closing metathesis as key steps.

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Discerning the role of spatially distinct components of mycobacterial membranes

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Abstract:

Mycobacterium tuberculosis, the etiological agent of tuberculosis, possesses an atypical cell envelope comprising of peptidoglycan-arabinogalactan complex with covalently bound mycolic acids (C₆₀-C₉₀) and lipids accounting for 40% of its dry weight. The cell envelope lipids are known to form an impermeable barrier against an array of antimicrobial drugs, aiding mycobacterial survival and resistance. The decisive role of each of the spatially organized lipid component of mycobacterial cell envelope is not yet fully understood. We aimed to isolate and study distinct components of mycobacterial envelope from *Mycobacterium smegmatis* mc²155 using steady state and time resolved fluorescence spectroscopy, atomic force microscopy, infra-red spectroscopy, and confocal microscopy to gain an insight into phase state behavior and nanomechanical properties of these lipids. These studies will pave way to design an effective mimic of mycobacterial membrane that can be used as a model membrane to test membrane perturbing activity of number of bioactive compounds.

Acknowledgements: We acknowledge funding support from Department of Biotechnology (Government of India), IRCC-IIT Bombay and DST-Inspire.

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Origin of stereinduction in the amination of alcohols using cooperative dual chiral catalysis involving chiral counter-ions

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Abstract:

Asymmetric catalysis using two chiral catalysts in combination using one-pot reaction conditions is in its early stages of development and understanding [^{1,2}]. We employ density functional theory computations to investigate the stereinduction in an asymmetric amination reaction of an alcohol catalysed by chiral phosphoric acid and a chiral Cp*Ir(diamine) [³]. First, the Ir–diamine complex is protonated by the phosphoric acid to form an ion-pair of the active catalytic dyad. Both chiral catalysts are involved throughout the catalytic cycle, thus constituting an important example of true cooperative catalysis. A borrowing hydrogen mechanism operates, wherein the phosphate abstracts the hydroxyl proton of the alcohol while the electrophilic Ir(III) simultaneously extracts the α -hydrogen to form a [Ir]–H species. The ketone thus derived from the alcohol through dehydrogenation condenses with aniline to form an imine. In the diastereocontrolling transition state, the hydride adds to the activated iminium, held in position in the chiral pocket of the catalytic dyad through a network of noncovalent interactions (C–H $\cdots \pi$, N–H $\cdots$ O and C–H $\cdots$ O) [⁴]. The enantioselectivity in this DYKAT process is identified as taking place at an earlier stage of the catalytic cycle prior to the diastereo-determining transition state [⁵].

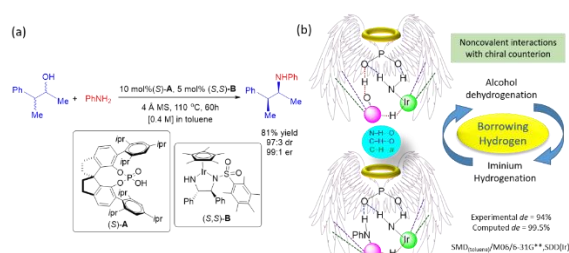


Figure 1. (a) Chiral counterion directed asymmetric amination of alcohol catalyzed by dual chiral catalysts; (b) Transition state models for crucial steps in the mechanism governed by noncovalent interactions of chiral counterion.

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An effective Hamiltonian formulation of EOM-CCSD for quasi-bound and bound anions

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Abstract:

Electronic resonances are nonstationary metastable states having ample amount of energy to break down into its constituents and enough lifetime to be characterised spectroscopically. Transient nature of these resonances cannot be well described in Hermitian quantum mechanics as they are designated by the formation of density of states in the continuum. The resonant states corresponds to the nonstationary solutions of time dependent Schrodinger equation and cannot be solved by conventional bound state quantum mechanical techniques. However, one can solve this problem by logical continuation of the Hamiltonian to the complex plane to achieve the square integrability of the resonance wave function using a complex absorption potential (CAP). The implementation of the CAP based EA-EOM-CCSD approach has already been described^{1,2} in the literature. However, the high computational costs of standard formulation of EOM-CCSD puts severe restriction on the size of the system to be studied. We have developed an effective Hamiltonian formulation of the EOM-CC method, which can provide an one electron description of the electron attachment process, with the higher order terms folded inside the one electron description. This approach can reduce the computational cost without significantly compromising the accuracy. We intend to use this approach to study the resonance induced radiation damage to genetic materials. The one electron picture offered by effective Hamiltonian formulation of the EOM-CCSD method makes it easy to interpret the calculated electron affinity in terms of physically meaningful quantities. We have developed a new energy decomposition scheme based on effective Hamiltonian formulation of EOM-CCSD method, which allows one to decompose the calculated electron affinity into its constituent component.

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Unravelling the Allosteric Regulation Mechanism of Formylglycinamidase synthetase

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Abstract:

Formylglycinamidase (FGAM) synthetase is a bi-functional enzyme from purine biosynthetic pathway. Here we are investigating the allosteric regulation mechanism controlled by a long flexible loop present approximately 30Å apart from the catalytic site. FGAM synthetase from *Salmonella typhimurium* encoded by *purL* gene (StPurL) is a single polypeptide of 143 kDa size, composed of glutaminase, FGAM synthetase, N- terminal and a linker domain [1]. Glutamine hydrolysis takes place in the glutaminase domain releasing ammonia. This ammonia is further migrated to the FGAM domain via a 25Å long hydrophobic tunnel where FGAR (*formylglycinamideribonucleotide*) to FGAM (*formylglycinamidineribonucleotide*) conversion happens [1]. The FGAR binding site is hypothesized to be capped by a long flexible disordered loop during the course of reaction [2]. To investigate the role played by this catalytic loop in allosteric regulation as well as in facilitating catalysis, mutational, structural, biochemical and molecular dynamics studies have been performed. Results show that any perturbations in the conserved region of the loop near the loop and N-terminal domain interface directly impacts the glutamine hydrolysis in glutaminase domain. The molecular dynamics studies were also performed in order to understand the role played by this loop in establishing the communication between the two active pockets. Results infer that loop adopts a disordered conformation during glutamine hydrolysis by showing maximum interactions with the N-terminal domain and facilitating the oxyanion hole movement towards the glutamine binding pocket to stabilize the tetrahedral intermediate formed during glutamine to glutamate conversion. In addition, the ordered conformation is adopted by the loop for capping the FGAR binding pocket during FGAM catalysis. Results also suggest that N-terminal domain is involved in signal transmission among both the catalytic domains for the reaction occurrence. This communication is established by a transient channel formation during partially ordered conformation of catalytic loop. The channel opens as a result of gate opening at the two extreme ends of the channel i.e. by breaking the interactions between R1263-S1052 at the top and H296-T310 at the end of the channel. FGAM synthetase is a key enzyme in purine biosynthetic pathway which is a potential therapeutic target for drug designing against microbes.

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Boosting the Magnetic Anisotropy of Prolate Single Ion Magnets Through External Electric Field

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Abstract:

Plenties of research has been done in the area of Single Ion Magnets to achieve a very high U_{eff} value for lanthanide complexes by designing proper ligand environment, maintaining symmetry around the metal centre, diamagnetic substitution or dilution experiment and through exchange interactions. Except very few reports, a study under an static external electric field (EEF) on the magnetic anisotropy has not been reported so far.¹ Effect of external electric field on any lanthanide complexes is a very challenging and recently a hot area to work in as very few studies are reported theoretically as well as experimentally. Both Erbium and Ytterbium are very well explored lanthanide ions in to exhibit excellent single-ion magnet properties, applying external electric field on the two complexes $\text{Li}(\text{THF})_4[\text{Er}\{\text{N}(\text{SiMe}_3)_2\}_3\text{Cl}]$ and $[\text{L}_2\text{Yb}][\text{Yb}\{\text{N}(\text{SiMe}_3)_2\}_3\text{Cl}]$ eventually lead to enhance the effective barrier height. *Ab initio* CASSCF-RASSI-SO-SINGLE-ANISO computation predicted a spin reversal barrier of 318 cm^{-1} and 1338 cm^{-1} at an electric field of 0.026 au and 0.028 au for the trigonal pyramidal Er^{III} and Yb^{III} complexes respectively.

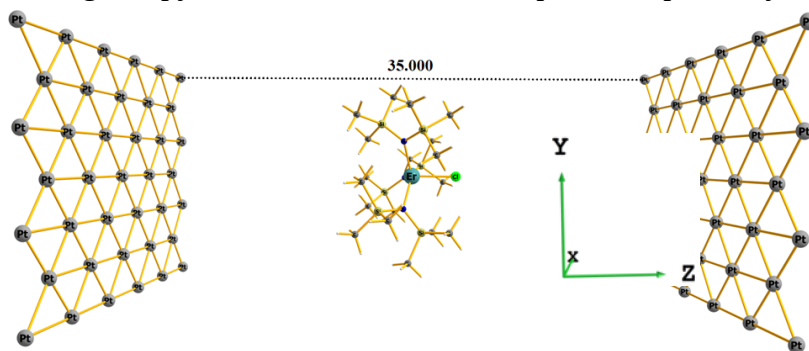


Figure: Arrangement of applying external electric field by putting point charges on two opposite Pt layers which are 35 Å apart and the molecule is at the centre.

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Theoretical Aspects of Proton Transfer Through Graphene

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Abstract:

Pristine graphene membrane was predicted to be impermeable to all nuclei at room temperature. However, recent experiments in the Geim group demonstrated fast thermal proton permeation rate through pristine graphene membrane. To obtain a mechanistic understanding, recent theoretical works included quantum effects of proton (tunneling and zero-point energy effects) using path integral methods, obtaining better experimental agreement. The nuclear quantum effects on the Arrhenius prefactor is still missing however. Additionally, most studies have looked at gas-phase proton permeation. Our work will explicitly treat the proton mode quantum mechanically and non-adiabatic reactive flux formalism will be used to compute the Arrhenius prefactor as well as include the effects of solvent modes.

**Effects of active fluctuations on energetics of a colloidal particle:
Super diffusion, dissipation and entropy production**

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Abstract:

We consider a colloidal particle immersed in an active bath ^{1,2,3,4} and derive a Smoluchowski equation that governs the dynamics of colloidal particle. We address this as active Smoluchowski equation (ASE). Our analysis based on this ASE shows a short time superdiffusive behaviour that strongly depends on the activity. Our model also predicts a non-monotonic dependence of mean energy dissipation ^{5,6} against time, a signature of activity-induced dynamics. By introducing a frequency-dependent effective temperature, we show that the mean entropy production ⁷ is time dependent and unlike a thermal system, it reaches a non-zero value in the long time limit. The prime reason for these anomalies is the absence of any FDT for our model of active noise. We also comment on how microscopic details of activity can reverse the trends for mean energy dissipation and entropy production.

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9. S. Chaki and R. Chakrabarti (To appear in *J. Chem. Phys.*, 2019)

P-11

Looking out for Green tea polyphenols

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Abstract

Protein condensation diseases render the study of their inhibition an interesting area of research. For example, amino acid modifications and/or aggregation in human γ -crystallin and other members of the crystallin superfamily are the main causes of cataract formation. *In vivo/in vitro* factors like ultraviolet (UV) radiation, pH, temperature and exposure to chemical agents result in a disruption of the structural integrity of the proteins. The ability of green tea polyphenols in the prevention of angiogenesis and the fibrillation of proteins shows their immense potential. A decrease in the extent of Trp residue oxidation of the cataractous human γ -crystallin in the presence of the major green tea polyphenol, (-)-epigallocatechin gallate (EGCG) has been observed. Recombinant human γ B-crystallin overexpressed in *E. coli* exposed to UV radiation under physiologically relevant conditions in absence and presence of different concentrations of green tea polyphenols show their potency against oxidative photodamage of the protein. The low pH and elevated temperature mediated aggregation of recombinant human γ B-crystallin confirms the amyloid like fibrillar nature of the human γ B-crystallin aggregate. It has been observed that disruption of the fibrillar network is possible with green tea polyphenols.

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Low Temperature Synthesis of K-substituted LaMnO₃ MicrocubesVishal Kotha¹ and Leela Srinivas Panchakarla^{1,*}¹ Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India.E-mail: vishal29raja@gmail.com, panchakarla@chem.iitb.ac.in**Abstract:**

LaMnO₃ (LMO) is an antiferromagnetic insulator but the substitution of La³⁺ by alkaline earth metals makes it ferromagnetic metallic system. Substitution of the La site in LMO by divalent cations (e.g., Ba²⁺, Sr²⁺, Ca²⁺) is known since last 5 decades. In these manganites unique phenomena like charge, spin and orbital ordering has been observed. But recently the discovery of colossal magnetoresistance (CMR) in these doped LMO has triggered the attention of scientific community. In these perovskite manganites Mn³⁺ to Mn⁴⁺ ratio leads to the insulator to metallic transition (IMT) and also the magnetic phase transition that too at above room temperatures. Instead of divalent alkaline earth metals the substitution of half of La³⁺ by monovalent alkali metal ions in rare earth manganites achieves equal amount of hole doping, because for the similar amount of aliovalent dopant the hole density becomes twice than that of the divalent ion doping. Till date these manganites have been synthesized above 600 °C. Here we present low-temperature solution based synthesis, structural characterization and magnetic properties of potassium substituted LMO perovskite phases in cubic shape.

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Clean energy production and thermal applications of graphene related 2D materials

Himanshu Chakraborty

Abstract:

Hexagonal borocarbonitrides (BCN) are a class of 2D materials, which display excellent catalytic activity for water splitting. We report superior hydrogen evolution activity of metal-free BCN catalysts. The highly positive onset potential (≈ 56 mV vs. RHE) and the current density of 10 mA cm^{-2} at an overpotential of 70 mV exhibited by a carbon-rich BCN with the composition BC_7N_2 demonstrates the extraordinary electrocatalytic activity at par with Pt. Theoretical studies throw light on the cause of high activity of this composition. The high activity and good stability of BCNs surpass the characteristics of other metal-free catalysts reported in recent literature.

Here, we report analysis of thermal stability, phonons and thermal conductivity of BCN monolayers over a wide range of temperatures using classical molecular dynamics simulations. Our results show that in contrast to the case of graphene and boron nitride monolayers, the out-of-plane phonons in BCN monolayers induce an asymmetry in the phonon density of states at all temperatures. Despite possessing lower thermal conducting properties compared to graphene and BN monolayers, the BCN nanosheets do not lose thermal conductivity as much as graphene and BN in the studied temperature range of 200-1000 K, and thus, the BCN nanosheets are suitable for thermal interface device applications over a wide range of temperatures. Besides their promising role in water splitting, the above results highlight the possibility of expanding the use of BCN 2D materials in thermal management applications and thermoelectrics.

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P-14

Anuj kumar

Abstract:

The structural transformation of double-stranded xyloNA and RNA were probed by modulating the dispersion energy. For the RNA the increase and the decrease in dispersion energy leads to over-winding and unwinding of the helix. These structural transformations resembles the features observed due to action of the enzymes topoisomerases and helicases, respectively. On the other hand, increase in dispersion energy has minimal effect on the structural transformation of double-strand xyloNA, whilst decrease in dispersion energy results in the structural transformation which happens due to the action of helicases. The unresponsive behaviour of xyloNA to increase in the dispersion energy is attributed to the presence of $Lp \cdots \pi$ interaction between the oxygen atom of the xylose sugar and the adjacent nucleobase.

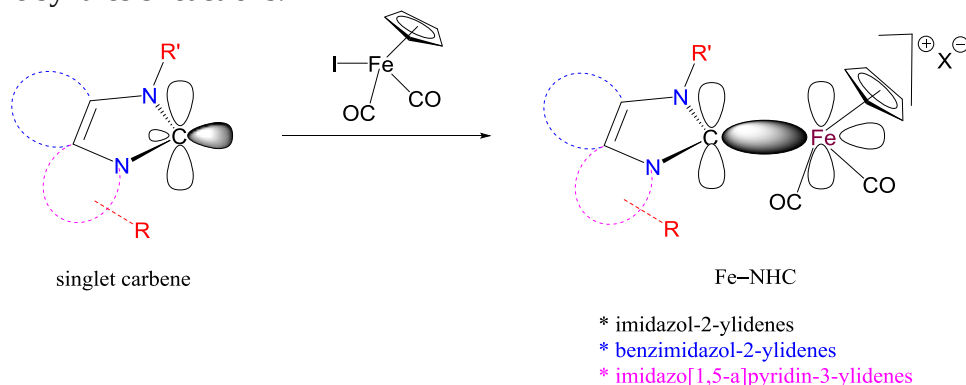
Studies of Iron and Ruthenium Complexes of N/O- Functionalized N-Heterocyclic Carbene Ligands in Homogeneous Catalysis

A. P. Prakasham and Prasenjit Ghosh*

Department of Chemistry, IIT Bombay, Mumbai – 400076, India

Abstract:

Iron is one of the most potential metal in catalysis that efficiently used in many catalytic transformations but with the NHC ligands remain overlooked. In order to explore the application of iron NHC complexes in catalysis, a series of cyclopentadienyl based cationic half-sandwich iron(II) N-heterocyclic carbene complexes with different structural backbone of the type $[\text{CpFe}(\text{NHC})(\text{CO})_2]\text{X}$, where NHC = imidazol-2-ylidene, benzimidazol-2-ylidene and the imidazo[1,5-a]pyridin-3-ylidene were synthesized and structurally characterized (Scheme 1). The catalytic potential of these $\text{Fe}^{\text{II}}\text{NHC}$ complexes were explored in various organic transformations like the hydrosilylation, asymmetric Michael addition and the α -enaminone synthesis reactions.



Scheme 1. Synthesized $\text{Fe}^{\text{II}}\text{NHC}$ complexes of various structural motifs.

In addition, different functionalized chelate N-heterocyclic carbene complexes of ruthenium, namely the amido and picolyl functionalized complexes have been synthesized from their respective silver carbene complexes through transmetallation reaction (Figure 1). The structurally characterized ruthenium complexes have been utilized as catalysts in the tandem α -alkylation of secondary alcohols.

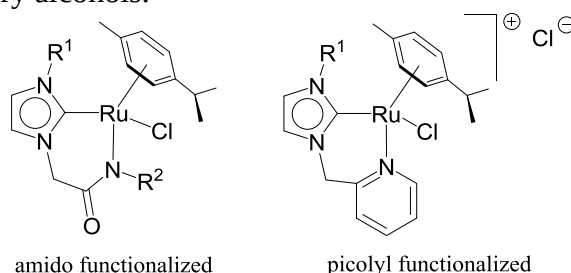


Figure 1. Synthesized functionalized Ru–NHC complexes of different structural motifs.

Lysine directed single-site labeling of native proteins

Dattatraya G. Rawale and Vishal Rai

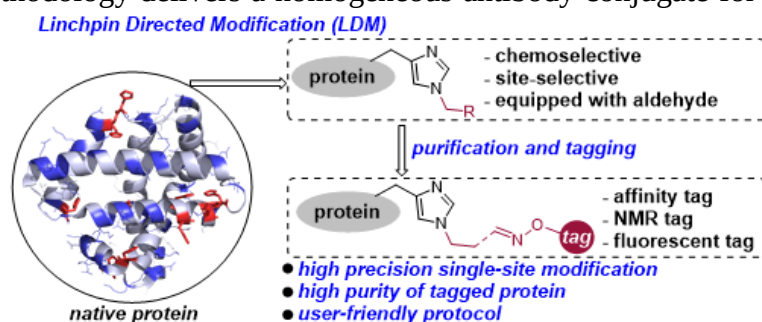
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Abstract:

The interest in precise labeling of protein has emerged from the necessity to understand and regulate their structure and function. However, the associated challenges led to the belief that required chemical methods would not be feasible. In this perspective, our initial breakthrough came from methods that distinguished reactivity of one residue from all the other proteinogenic residues.^{1,2} Recently, we were able to demonstrate a modular chemical platform that enables precise single-site labeling of native proteins, enzymes, antigen, and monoclonal antibody through linchpin directed approach.³ We designed a reagent with three components: aldehyde (F_K), epoxide (F_H), and spacer. The F_K (linchpin) reacts rapidly, reversibly, and chemoselectively with all the accessible Lys residues. Subsequently, the F_H renders relatively slow, irreversible, and chemoselective reaction with a His residue. The spacer is designed to regulate the inter-functional group distance. The method allows single-site labeling of His residues of multiple native proteins. The reagent design allows the labeling of distinct sites in a protein with exclusive selectivity. The technology can be further applied to label a single protein in the presence of other proteins. The LDM platform provides the first ever modular tool for single-site labeling of native proteins. It regulates the desired pathway through an intramolecular route, while the undesired pathway traverses through an intermolecular route. The F_K enables an easy purification of the labeled protein. This multi-tasking group (F_K) enables the late-stage bio-orthogonal attachment of NMR tag, an affinity tag, and a fluorophore. Importantly, the structure and function of the labeled proteins and enzymes remain unaltered. The methodology delivers a homogeneous antibody conjugate for directed

cancer chemotherapeutics.



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Unfolding the role of fluctuation in neural stem cell fate decisions

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Abstract:

A precise coordination between self-renewal and differentiation of neural stem/progenitor cells should be maintained for proper development of nervous system. These progenitor cells further influence each others dynamics by interacting through several extra and intracellular signaling pathways (Shimojo et al. *Neuron* 2008, Sengupta et al. *ACS Chem. Neurosci.* 2018), while the factors that specifically govern the cell fate decision making process remain elusive. Intriguingly, recent studies (Philips et al. *eLIFE* 2016) suggest that this cell fate decision making events in neural stem cells are highly stochastic in nature. To unravel the factors regulating the dynamics of neural stem cell fate decision making events, we have constructed a stochastic mathematical model that enables us to investigate the influence of different sources of heterogeneities that organize the development in stem cells under fluctuating cellular environment. Our stochastic simulation shows fluctuation in the signaling pathway helps neural progenitors to take the decision of symmetric and asymmetric cell division. By analyzing this stochastic mathematical model, we are trying to put forward a hypothesis for the complex neural cell fate determining process that can be examined and validated with currently available experimental observations or specifically designing new experimental setup.

Hybrid Soft Biomaterials from Colloidal Building Blocks

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D. Singh, and K. P. Sharma*

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Abstract:

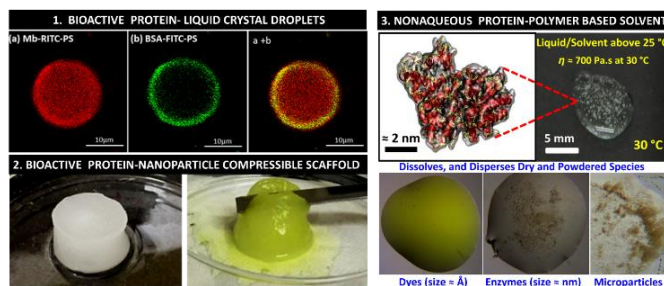
Design and development of multi-functional, hierarchically structured, and highly ordered materials is the key to the advancement in the field of materials nanochemistry, and bionanotechnology. These fields are likely to play an important role in driving markets, and economies in the developing countries by fulfilling their high demand towards the improvement in health, and energy sector. Specifically, the formation of biodegradable materials with novel properties, multiple functions, improved efficiency, and higher sensitivity can cater to the demand of health and diagnostics industry. In this context, biomaterials fabricated using proteins/enzymes are the focus of much attention since these provide highly advanced functions, and properties which can be used for variety of applications in bioelectronics, bio-sensing, drug delivery, bio-catalysis and bio-nanocomposites. However, the road to the realization of such a class of biomaterial involves combining/incorporation of proteins/enzymes with other type of functionalities in the form of polymers (synthetic, and natural), surfactant, nanoparticles, liquid crystals, etc. In most cases this leads to denaturation, or unfolding of the protein/enzymes, and ultimately lost of their structure, and function. Clearly, a combination of both structure and function can provide high performance biomaterials in the form of films, hydrogels, nanoparticles, and fibres for use in various applications.

In our lab we combine efforts with the help of bio-conjugation techniques to stabilize proteins/enzymes via surface re-engineering with polymers to form hybrid bioconjugates. These bio-conjugates can thus be used as make new class of materials, as standalone,^{1,4} or by integrating with structurally and functionally compatible components such as liquid crystal droplets,² ionic liquids,⁵ and colloidal particles.^{3,6} In a significant advancement, we have shown that surface modification of proteins with polymer surfactant matches miscibility with hydrophobic liquid crystal (LC) droplets to provide spontaneous sequestration of biomolecules into LC droplets to form a new class of soft material having LC optical signature and bio-functionality retained from proteins.² Recently, we have also shown development of sturdy, robust, enzymatically active biocatalytic sponges fabricated using ice templating an aqueous mixture of nanoparticles and core-shell enzyme-polymer surfactant bioconjugates. These core-shell bioconjugates based sponges exhibit mechanoresponsive and recyclable catalytic behaviour with the capability of tuning the rate of reaction by changing the frequency of compression-decompression of the sponge.³ In an another example, a new class of composite liquid comprising enzyme bioconjugates and hollow mesoporous rods having intrinsic porosity in the liquid state, has been fabricated. Carbon dioxide can be sequestered in the porous liquid, and subsequently catalytically converted into carbonates using carbonic anhydrase enzyme.⁶

Overall, we envisage in developing and contributing significantly to advancing a new area of biomaterials engineering at the interface with soft matter chemistry which will directly, or indirectly help in solving scientific challenges, and problems in various industries involved in pharmaceutical, detergency, cosmetics, paints, health, and diagnostics.

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Highly Porous and Ph Responsive Hydrogel Beads of Bovine Serum Albumin for Efficient Removal of Organic and Inorganic Components from Water: Smart Nanofactories for Water Remediation

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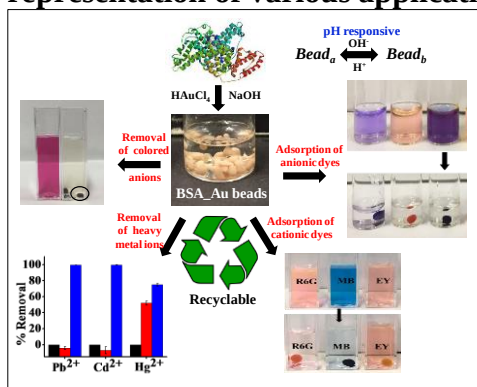
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Abstract:

One of the major crises in the world today is the availability of potable drinking water. Therefore, it is important to develop efficient systems to remove contaminants, such as, toxic metal ions and organic dyes. Protein based hydrogels serve as one of the best systems as the same does not impart any toxicity to the water. Moreover, the porous nature of the hydrogels is an added advantage. In view of the same, a readily available protein, bovine serum albumin (BSA) has been employed to synthesize novel hydrogels/beads via unprecedented strategy. The red fluorescent BSA_Au NCs upon acid treatment aggregates to forms bead like structures. These beads are stored separately in acidic medium (*Bead_a*) and basic medium (*Bead_b*). These beads are highly porous and are Ph responsive. The *Bead_a* shows specific and very high adsorption for anionic dyes and colored anions while *Bead_b* shows specific adsorption of cationic dyes and toxic metal cations. These beads being Ph responsive can desorb the adsorbed dye when the Ph of the medium is altered and therefore allowing it to be recycled and reused. These beads have also responded positively to removal of toxic heavy metal ions and colored anions from water with high efficiency. Therefore, these BSA-beads can be very well utilized for the purification of water from organic and inorganic components and serves to be important in water remediation.

Figure 1- Schematic representation of various applications by BSA-beads



Synthesis of coordination complexes for application towards molecular magnetism, catalysis, electronic devices (GFET) and detection of Parkinson's diseases.

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Abstract:

Our group interested in the synthesis of coordination complexes of the various transition metals and inner- transition metals. Coordination complexes are widely used in many areas. One of our area of research is molecular magnetism where we design and synthesize both multinuclear and low coordinate mononuclear complexes of desired magnetic properties. We use wide range of ligands to isolate molecules of different nuclearity. For multinuclear complexes we used ligands having different pockets available for coordination, while we use sterically hindered ligands for low coordinated complexes. The main purpose of working in this area is that these molecules can be used as potential information storage devices, molecular qubits (quantum computer) and magnetic coolants which is much cheaper source for reaching to lower temperature compared to liquid helium. Other research interests involve making electronic devices (GFET) by functionalization of appropriately design molecules on the surface of graphene and carbon nanotube. In addition to this we are also actively involved in the synthesis of highly reactive redox active 3d-metal complexes and their catalytic application towards various transformations (hydrophosphination, hydrosulphonation, halogenation of cycloalkenes, conversion of CO₂ to methanol). Also, our research focuses on developing organic/inorganic or hybrid fluorophore to detect, not only the mature fibrils but also the toxic oligomers, which will facilitate to understand the disease progression in its early stage. Besides, we also aim to develop new small-molecule therapeutic strategies against this neurodegenerative disorder."

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Blinking and Spectral Dynamics of Individual Perovskite Nano-/Micro-Crystals

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Single-Emitter Spectroscopy and Dynamics Group at Department of Chemistry, IIT Bombay

Abstract:

All inorganic and organic-inorganic (hybrid) halide perovskites have shown tremendous progress in light to energy conversion efficiencies. These materials exhibit an array of useful properties such as ambipolar charge transport, high absorption coefficient and emission yields as well as excellent charge carrier diffusion lengths/coefficients, which make them ideally suited for both photovoltaic and light emissive device applications. While the bulk (ensemble) properties of these materials have been studied extensively, the optoelectronic behaviors of individual nano- and micro-crystals are still unclear, primarily because these materials can have considerable heterogeneity not only in terms of both composition and size, but also in terms of carrier migrations/recombination dynamics and photoluminescence emission characteristics. Here, we discuss a few interesting observations on the photoluminescence intermittency (blinking) and temporally-random spectral fluctuations (spectral diffusion) of individual nano-/micro-crystals of hybrid halide perovskites. Spatially and temporally-resolved emission spectroscopy measurements on these nano-/micro-crystals allow us to investigate the heterogeneity in both blinking and spectral diffusion behaviors, the understanding of which can potentially be useful for these materials to be used for device applications. This presentation provides an overview on single-emitter studies in our group in light of some surprising results on hybrid-halide perovskites.

Recent Research Activities of R. Murugavel's Research Group

Members of RM Group

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Email: rmv@chem.iitb.ac.in**Abstract:**

Research work carried out in our group deals with several important aspects of inorganic-organic and organic materials chemistry such as: (a) single-molecule and single-ion-magnets (SMMs and SIMs) with emphasis on 4f and 3d metal ions,¹ (b) developing synthetic strategies for thermally unstable precursors for ceramic phosphates starting either from dialkyl or monoalkyl-phosphates,² (c) new synthetic strategies for porous metal, covalent, and metal-covalent organic frameworks (MOFs, COFs and MCOFs) for the applications of sensing, gas storage and catalysis,³ (d) chemo-sensory materials for chemically inert (*i.e.* polynitroaromatic explosives) to highly reactive analytes (*i.e.* anions) which are considered to be hazardous,⁴ and ϵ sterically encumbered phosphorous heterocycles. We have unraveled importance of parameters such as choice of metal precursor, choice of organic groups on ligands and inclusion or exclusion of an ancillary donor ligand to engineer the zeolitic secondary building units (SBUs) such as D4R, D6R, D8R and 8-connected D4R.⁵ We are currently developing strategies for self-exfoliating layered materials which on soft sonication can produce truly single layer 2D materials. A brief description of our recent contributions to the above-mentioned areas is going to be presented in the poster.

We thank DST (SERB) for the financial support and all IIT-B instrumentation facilities for spectroscopic and analytical data.

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Enhancement of photocatalytic activity and photo-stability of MoS₂ by making composites with other semiconducting materials

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Abstract-

Heterogeneous photo-catalysis has received significant attention for the water purification and hydrogen generation. Hydrogen evolution from water i.e., water to hydrogen conversion in the presence of solar energy is one of the most favorable method for getting a pollution free and renewable fuel and this is a great challenge for the environment sustainability (1). However, there is a possibility for improvement in the currently reported photo-catalysts like enhancement of light absorption range, reduction of photo-corrosion, low cost and high efficiency and stability (2). Some approaches were made to increase the stability and performance of these catalysts includes making composite with other semiconducting material or application of passivation layer to increase the life-time of exciton. We have previously reported MoS₂ composite with Mo₂N to overcome the problem associated with a bare catalyst (3). This work reports MoS₂ composite with other semiconducting material as well as with reduced graphene oxide (rGO) would be better for photo-electrochemical activity and stability. The synthesis, characterization and photo-electro catalytic evaluation of these materials will be presented.

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Fatty Amine Conjugated Cationic Bovine Serum Albumin Nanoparticles Exhibit Antifouling and Target-Specific Hydrophobic Doxorubicin Delivery Properties

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Abstract:

Protein based nanostructures has reformed the nanoscience and nanotechnology on the account of their smaller sizes and greater surface areas, which instigates their interactions with other molecules. The protein nanoparticles (NPs) have better biocompatibility, biodegradability and also have the easy access for additional surface modifications. These NPs have been successfully used as drug delivery system with increased bioavailability and reduced toxic side effects of the drug molecules. Herein, we report a simple approach to formulate fatty amines conjugated cationic BSA (FCBSA) NPs by conjugating laurylamines to the BSA protein. The small positive nanoassembly surface of FCBSA exhibit high stability against thermal, pH, and proteolytic enzyme stresses. The FCBSA demonstrated excellent biocompatibility against both normal and cancer cell lines. The nanovehicles efficiently encapsulate hydrophobic anticancer drug, doxorubicin (Dox) and shows controlled release property, human blood serum stability, antifouling property and higher binding affinity for the anionic membranes. Furthermore, the cellular studies also showed that biotin tagged cationic FCBSA (bt-FCBSA) can efficiently deliver Dox to the biotin receptor-positive HeLa cells leading to significant cell death. Overall, an easy access to the fatty amines modified cationic protein NPs with their surface modification capabilities could be eminent candidates for both passive and active targeted delivery of anticancer agents.

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Ambient Triplet Harvesting from Donor-Acceptor Naphthalene Diimides: Evidence of Dual Delayed Fluorescence and Red-emitting Room Temperature Phosphorescence

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Abstract:

Red to NIR emitting room temperature phosphorescence (RTP) and thermally activated delayed fluorescence (TADF) is very challenging and extremely important for realizing high efficient white TADF-OLEDs.¹ In that regard, Monkman and co-workers established the importance of spin-vibronic coupling in designing efficient TADF materials with suitable triplet energy in order to enhance ³CT (charge transfer) and ³LE (locally excited) mixing.² Thus, investigations on low triplet energy donor or acceptors is necessary to achieve efficient red emitters. Recently, we have studied core-substituted naphthalene diimides (cNDIs, known for low ³LE energy) and stabilized triplet excitons in water to achieve ambient RTP utilizing a novel supramolecular self-assembly strategy.³ Interestingly, we observed unique anion- π based CT emission in the orange-red region independent of triplet emission resulting in phosphorescence, hinting towards the possibility of rISC process. Inspired from these observations we have synthesized a series of donor-acceptor cNDI molecules and observed deep red and NIR emitting TADF. We also observed that the donor (carbazole) attached directly to acceptor (NDI core) leads to weakly emissive twisted intra-molecular charge-transfer (TICT) state with extremely low PLQY (<1 %). However, TDDFT calculations suggests that a simple phenyl spacer between the donor and acceptor moieties is enough to increase the oscillator strength and minimize the TICT effect. As expected, an introduction of phenyl spacer increased the emission intensity by several folds and with excellent TADF emission. Detailed temperature dependent lifetime and emission spectroscopy showed possibility of efficient RTP along with TADF in our system. Since, the phenyl spacer improves the HOMO-LUMO overlap of the molecule, an increase in ΔE_{ST} is expected and thus a slower rISC rate (typical lifetime 80-150 μ s in air) is observed. Thus, suitable donors are under investigation to decrease the ΔE_{ST} gap and getting red to NIR TADF from cNDIs with better PLQY and shorter lifetime. Furthermore, we are working extensively on side chain functionalization at the imide position of NDI to obtain TADF organogels for solution-processable TADF-OLEDs. As cNDIs are an excellent class of materials in organic electronics because of their tunable redox properties, photo-stability and high charge-mobility; efforts towards understanding this class of materials is going to be really important for realizing advanced triplet exciton applications in near future.⁴

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400076*

Abstract:

Recent years have witnessed a significant growth in the area of low-valent main group compounds due to their potential to activate small molecules. However there is paucity of examples of low-valent main group compounds being used as a single site catalyst for organic transformations. This study represents the hydroboration and cyanosilylation reactions of a range of aldehydes by benz-annulated heavier N-heterocyclic germylene (**1**) and stannylene (**2**) under mild conditions. A wide variety of substrate scope was studied. The mechanistic pathway of cyanosilylation reaction initiates through the coordination of TMSCN with the catalyst followed by the attack of aldehydes. Conversely, hydroboration proceeds via formation of donor-acceptor adduct between HBpin and catalysts. Experimental and theoretical studies were performed to establish the mechanism

Rhodium-Catalyzed Denitrogenative Insertion Reactions of *N*-Sulfonyl-1,2,3-triazoles

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Abstract:

The seek for the discovery and development of novel and efficient synthetic approaches for accessing heterocyclic scaffolds relevant for biological studies and medicinal applications is at the fore front of organic chemistry. In the past few years, transition-metal catalyzed denitrogenative ring opening of *N*-sulfonyl-1,2,3-triazoles and exploiting their reactivity in the construction of other heterocyclic compounds gained a lot of interest.¹ Various transition-metals like Rh, Cu, Ni and Pd were able to trap the α -iminodiazole intermediate and convert it into a highly reactive α -iminocarbenoid species, which shows reactivity similar to classical metal-carbenoids generated from diazoacetates. In addition, these species also display unique reactivity leading to a variety of novel reactions like transannulation, cycloaddition and insertion reactions. In this presentation, I would like to discuss our efforts to exploit the reactivity of Rh-azavinyl carbenoids in a variety of insertion reactions to prepare various heterocyclic moieties like oxazolidinones,² benzoxazinones³ and indigoids.⁴

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Phosphorus Based Ligands: Synthesis, Transition Metal Chemistry and Catalytic Applications

Prof. M. S. Balakrishna's Group

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Abstract:

Ligand design plays an important role in coordination chemistry and catalysis.¹ Phosphorus based ligands are of increasing interest in transitional metal chemistry and homogenous catalysis owing to the properties they confer to their metal complexes, which in turn facilitate a variety of organic transformations. We have been actively engaged in the coordination chemistry of functionalized phosphorus-based ligands.²⁻⁷ A library of phosphine ligands have been synthesized in our laboratory (Chart 1). The interactions of these ligands with appropriate transition metal precursors resulted in the formation of simple mononuclear complexes to novel 1 or 2-dimensional coordination polymers. The synthetic details, structure and bonding aspects, reactivity and catalytic applications of some of these systems will be presented.

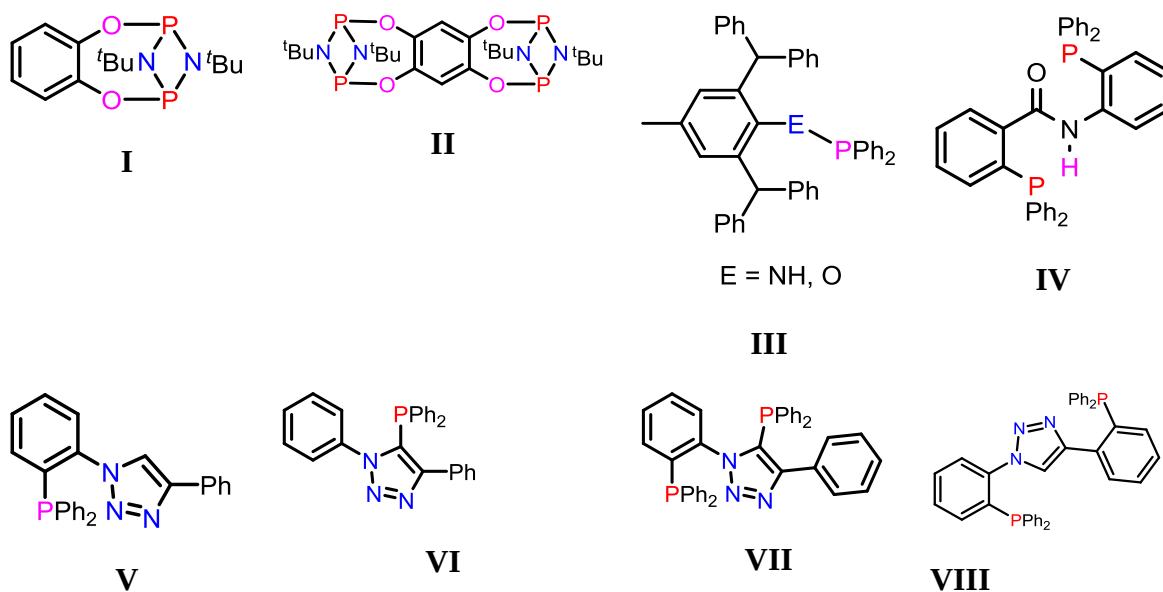


Chart 1. Phosphine ligands synthesized in our laboratory

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Synthesis of Macrocyclic Scaffolds for Gated Ion Transport

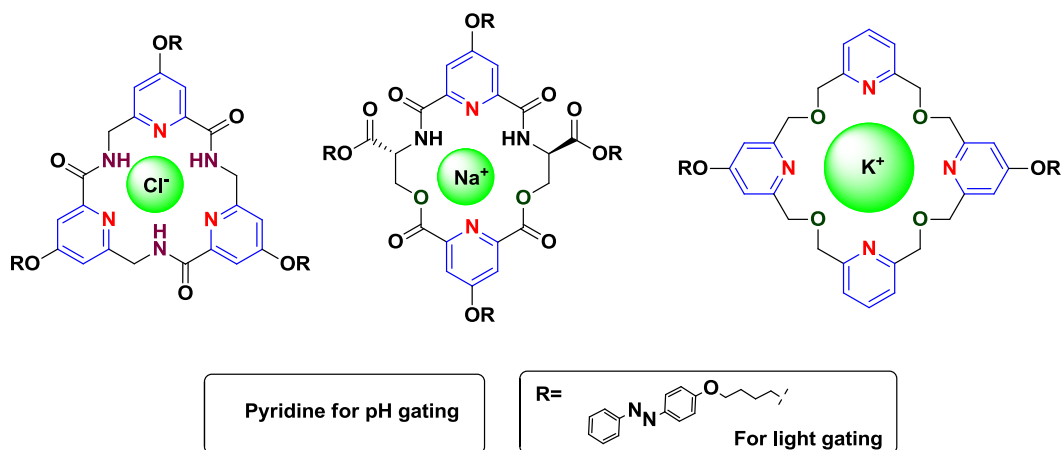
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Abstract:

Ion transporters are vital for biological processes such as maintaining ion concentration and cell volume.¹ Synthetic ion transporters that are stable *in vitro* are promising candidates for use as therapeutics and sensors.^{2,3} In particular, macrocycles with suitable functionality are attractive scaffolds for selective ion-binding. Several macrocycles such as crown ethers,⁴ calixarenes,⁵ cyclic peptides,⁶ calixpyrroles⁷ and porphyrin-based organic cages⁸ are known scaffolds for ion transports. Our group has synthesized pyridyl derived triamide,⁹ ester-amide,¹⁰ and ether¹¹ macrocyclic scaffolds that show selective transport for chloride, sodium and potassium ions, respectively. These macrocycles are pH sensitive because of the basic pyridine units within the scaffold. They can also be made photo-responsive by attaching light sensitive groups on the periphery.



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Supramolecular complexation of (N-methylpyridyl) Porphyrin with Sulfobutylether- β -cyclodextrin: Effective Photosensitizing Behavior

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Abstract:

Porphyrins, especially the 5,10,15,20-tetrakis(4-N-methylpyridyl) porphyrin (TMPyP), are well accepted as photosensitizers due to strong absorption from visible to near-infrared region, good singlet oxygen quantum yields as well as chemical versatility, all of which can be further modulated through planned supramolecular strategies. In the recent past, several attempts have been made to functionalize the host and/or the guest molecules to control and tune the host guest interactions for targeted applications. In this context, sulfobutylether- β -cyclodextrin (SBE₇ β CD) a chemically modified cyclodextrin moiety with a structure designed to optimize the solubility and stability of drugs has received much attention.^[1] In this study, we report the construction of supramolecular assembly of TMPyP dye/drug with SBE₇ β CD macrocycle through host-guest interaction. The availability of four cationic N-methylpyridyl groups favors multiple binding interactions with the SBE₇ β CD host, building an extended supramolecular assembly of SBE₇ β CD and TMPyP. In addition to the spectroscopic characterizations for the assembly formation, the same has been pictured in SEM and FM images. Complexation of TMPyP has brought out beneficial features over the uncomplexed TMPyP dye; enhanced fluorescence intensity and lifetime, singlet oxygen yield and improved photostability. All these synergistic effects of supramolecular assembly of SBE₇ β CD:TMPyP make the system as an effective photosensitizer.

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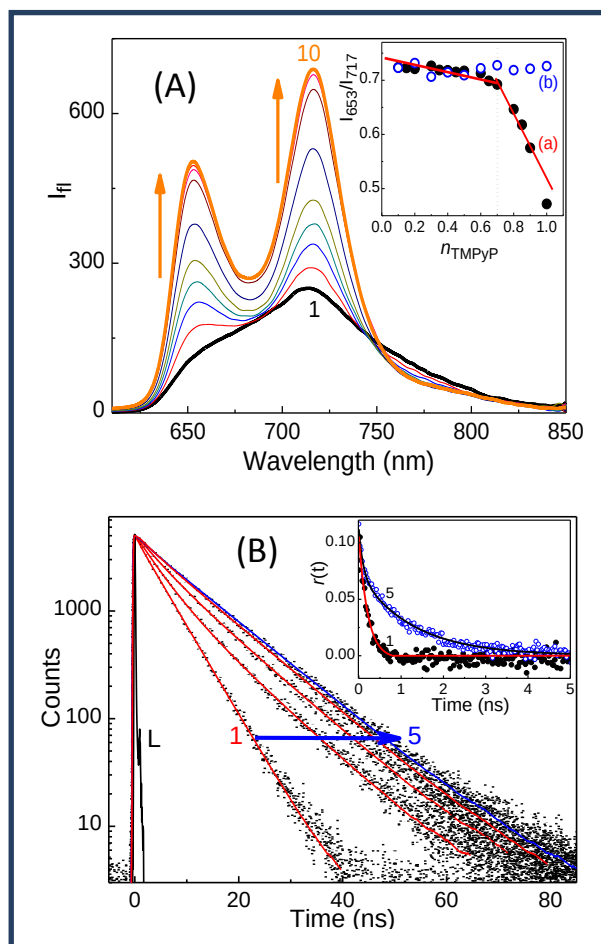


Figure1. (A) Fluorescence spectra and (B) Fluorescence decay traces of $\sim 2 \mu\text{M}$ TMPyP solution at different concentrations of SBE₇ β CD. The inset displays (A) Jobs plot using the fluorescence intensity ratio and (B) fluorescence anisotropy traces: 1) TMPyP and 2) Complex

Synthesis of AAT Containing Zwitterionic Oligosaccharides

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Abstract:

2-Acetamido-4-amino-2,4,6-trideoxy-D-galactopyranoside (AAT) is present on the cell surface of many bacterial polysaccharides such as *Shigella sonnei*,¹ *Streptococcus pneumonia*,^{2,3} *Bacteroides fragilis*,^{4,5} and *Streptococcus mitis*.⁶ Recent studies on zwitterionic polysaccharides revealed that they can elicit a T-cell dependent immune response, mainly due to the positive and negative charges present on them. In these species, positive charge originates from the 4-amino functionality whereas negative charges comes from the phosphate or ester groups. To understand the specific function of AAT containing polysaccharides in drug or vaccine therapy, one needs access to pure compounds for biological studies. one of the main challenges is the synthesis of AAT building block.

Recently our lab established an expedient and one pot protocol to synthesize AAT building blocks from cheaply available D-mannose in few steps with good yields.^{7,8,9,10} The short and efficient methodology was applied for the synthesis of O-linked tetrasaccharides of *Bacteroides fragilis* PSA1¹¹ and trisaccharide of *Streptococcus pneumonia* SP1.

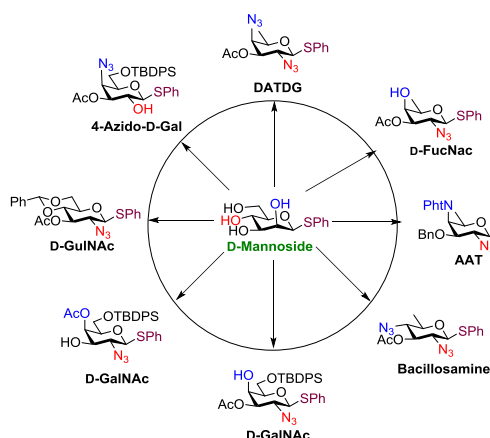


Figure 1. Synthesis of various rare sugar building blocks.

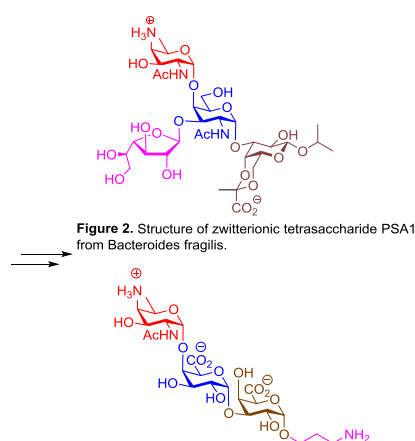


Figure 3. Structure of zwitterionic trisaccharide from streptococcus Pneumonia SP1.

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Fundamental Understanding the Efficiency of Various Ionic Liquids and Deep Eutectic Solvents: towards Dissolution of Bio-Macromolecules

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Abstract:

The disintegration of biomacromolecules into its simpler molecules has been a long term research topic to enhance their applicability as new therapeutic agents for treating various diseases and understand their complex structures [1]. At CSIR-CSMCRI, successful efforts are being made to solubilize biomacromolecules such as DNA, chitin, spider silk, guar gum etc., in various ionic liquids (ILs) and deep eutectic solvents (DESs) [2-4]. During the course of the work it was observed that, the different biomacromolecules are soluble in different extent in ILs and DESs. To figure out the difference, biomacromolecules (e.g. DNA and polylysine) have been used for dissolution in ILs and DESs having same cations and anions. As a result, different dissolution profile for DNA and polylysine was obtained. In order to understand the fundamentals of the dissolution phenomenon of biomacromolecules in ILs and DES, we started to compare the physicochemical properties of ILs and DESs having similar constituents. The solute-solvent interactions cannot be defined with single physical parameters satisfactorily. Keeping this in mind the physicochemical properties of neoteric solvents like polarity, viscosity, diffusion, ionic conductivity and enthalpy of solution have been studied at room temperature as well as function of temperature.

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P-33

Seeking a road-less travelled in Pasteur's quadrant : from fundamental to applications using nanomaterials

Past and present members of Nanostructured Materials group (PI : Dr. C. Subramaniam)

This poster presents the various directions that are currently being explored by the group with respect to new materials, utilization of in-situ spectroscopic and microscopic techniques and development of platform-technologies. We seek to explore and identify structure-process-property-application correlation using existing nanomaterials. Our simultaneous attempts to fabricate novel nanostructured materials with tailored and controllable morphologies and surface chemistry are also highlighted. The knowledge and insights thus gained would be employed to develop various devices and platform-technologies such as:

1. Self-sustaining, wearable and mechanically robust energy storage platforms for storing electrical energy and power point-of-care devices such as diagnostics and location transmitters catering to Internet-of-things.
2. Electrode-electrolyte interface engineering to achieve seamless charge-transfer and thereby access ultra-high charge-discharge capability and power densities for energy-storage applications.
3. Understanding the role of support-catalyst interface in electrocatalytic processes through operand spectroscopy for rationale designing of energy-efficient catalytic systems
4. Molecular-level designing and implementation of dopants for two-dimensional materials for applications in low-power field-effect transistors and high-frequency logic inverters.
5. Point-of-care electrochemical platforms for qualitative and quantitative estimation of analytes ranging from soli nutrients (NPK) to physiological (muscular stress, blood pressure) parameters.
6. Designing nanostructures for solar-to-thermal heat conversion for water purification and thermally-conductive polymer nanocomposites for thermal-interface materials
7. Low-power, portable water desalination prototypes through capacitive deionization.

The poster seeks to highlight our approaches in these directions and present a brief overview of the results.

Synthesis and biophysical evaluation of G-quadruplex stabilizing and i-motif destabilizing molecules

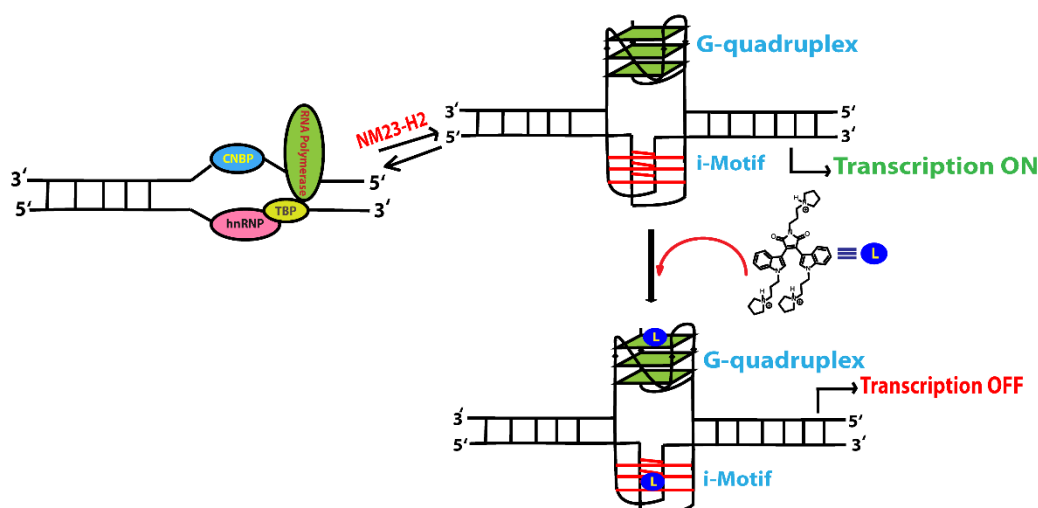
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Abstract:

G-quadruplexes (G4), four stranded motifs formed by G-rich DNA/RNA sequences found in the genome of both prokaryotes and eukaryotes.¹ Complementary C-rich sequences can form i-motif structures (iM) through hemi-protonated C-C⁺ base pairing.² These highly dynamic secondary structures can regulate a variety of biological processes such as replication, transcription and translation.³ Herein, we report the synthesis and biophysical evaluation of bisindolylmaleimide derivatives as novel G4/iM interacting molecules. The CD titration and melting experiments have shown that the lead molecule can act as an G4 stabilizer and as an iM destabilizer. Our results show the emergence of a new class of molecular scaffolds for both therapeutic and diagnostic applications centred around G4/iM structures.



Regulation of transcription by G4 and i-motif structure interacting molecules

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The effect of antibody F11.2.32 binding on the activity of HIV-1 Protease

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Abstract:

HIV-1 protease is an essential enzyme in the life cycle of the HIV-1 virus and thus a prime therapeutic target for the structure-based drug design. The conformational dynamics of the flap region of the protease is critical for the ligand binding mechanism, as well as for the catalytic activity. The F11.2.32 is a monoclonal antibody raised against the HIV-1 protease that inhibits protease activity on binding. We have studied the conformational dynamics of HIV-1 protease in its free and antibody bound forms using molecular dynamics (MD) simulations. In our results, we find that upon Ab binding to the epitope region (36-46) of HIV-1 protease, the overall flexibility of the protease is decreased including the flap region and the active site. This suggests an allosteric mechanism to inhibit protease activity. The protease mutants G40E and G40R are known to have decreased activity and were also subjected to MD simulations. It was found that the loss of flexibility in the mutants is similar to that observed in the protease bound to the Ab. Thus, the dynamical changes in protease could modulate the functional properties of the active site and thus the relative binding affinities for substrates and inhibitors. These insights highlight the role played by dynamics in the function of the protease and how control of flexibility through Ab binding and site specific mutations can inhibit protease activity.

Unravelling mechanism of resistance conferring methyltransferases

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Abstract:

Modifications at specific positions in ribosomes by the methyltransferases is one of the most prevalent strategy adopted by the pathogenic bacteria's to circumvent the lethal actions by plethora of antibiotics. Our work focuses on Erm (erythromycin resistance methyltransferases) enzymes which mediate the S-adenosylmethionine dependent Rna methylation at A2058 position leading to macrolide, lincosamide and streptogramin resistance. To decipher the determinants that probably govern specificity in these enzymes we performed mutagenesis studies involving alterations in the loop regions in a model system KsgA, a housekeeping methyltransferase. Studies revealed that chimeric constructs with specific embellishments on the basic Rossman fold showed Erm like behaviour in vitro as well as increased the tolerance towards macrolide in vivo. Owing to their significance in substrate recognition, these structural elements in the catalytic domain can serve as a unique target for the development of Erm specific inhibitors. To further understand how Erm binds to the RNA and brings about base flipping, we have exploited the nucleobase surrogates thienoguanosine and aminopurine incorporated at the different position in small RNA substrate mimic. Changes in the fluorescence were observed at A2058 upon binding of Erm signifies the base flipping mechanism. The binding also provoked conformational changes in residues present in the vicinity of A2058. The findings from stop flow studies provided further mechanistic insights into Erm-RNA interaction which involves at least three steps process.

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P-37

Aggregation of poly(*p*-phenylene terephthalamide) chains: Emergence of fiber defects

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Abstract:

Some of the strongest polymer-based fibers are obtained by processing a nematic solution of poly-*p*-phenylene terephthalamide (PPTA) in concentrated acid. Molecular dynamics simulations reveal that the lateral density of PPTA chains in the acid solution is inhomogeneous on scales shorter than the persistence length. Hairpin turns, insertions, and other defects are stabilized by chain-chain contacts. These results suggest a mechanism of fiber assembly through coalescence of nanofibrils, and an explanation for the limited strength of PPTA fibers even at high crystallinity.

Diverse functionalization of alkynes for the synthesis of heterocycles

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Abstract:

Metal catalysed transformations of alkynes have gained prominence for the synthesis of *oxa*- and *aza*-cycles. However, their utility under metal free conditions is still under explored. In a program directed at the stereoselective synthesis of *oxa*- and *aza*-cycles, we demonstrated that the oxonium and iminium ion intermediates generated from vinylogous carbonates and carbamates in the presence of Lewis acids can be trapped with alkynes giving 2,3-disubstituted dihydrobenzofurans and indoline derivatives.^{1,2} The regioselectivity of alkyne iminium ion cyclization can be reversed using a tethered hydroxy group as nucleophile. We have also developed divergent synthesis of *N*-fused indolyldine, indole, and indoline derivatives using alkyne-iminium ion cyclisation. Interestingly, trapping of vinyl cation intermediate generated after alkyne iminium ion cyclisation was found to be dependent on the Lewis/Brønsted acid and solvent used.³ *N*-propargyl indoles were also used in the synthesis *N*-fused indoline and indole derivatives under radical cyclization conditions as well as under Lewis acidic conditions.⁴⁻⁵ Lewis acid mediated multi-segment coupling cascade for the synthesis of densely substituted 4-alkoxy quinoline *via* an oxonium ion triggered alkyne carboamination sequence involving C-C and C-N bond formations was developed.⁶ We have developed Lewis acid mediated segment coupling of alkynes with aromatic aldehydes for the construction of cyclic ether-fused chromenes.⁷ Further, Lewis acid mediated ‘*endo-dig*’ hydroalkoxylation-reduction on internal alkynols gave rapid access to the cyclic ethers and 1,4-oxazepanes in a stereoselective fashion.⁸ Recently, we have used tandem radical cyclization on alkynyl vinylogous carbonates for the synthesis of tertrasubstituted furans/dihydrofurans.⁹

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P-39

**Physicochemical Insights into the Stabilization of Stressed Lysozyme and Glycine
Homopeptides by Sorbitol**

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Abstract:

Understanding the mode of action of osmolytes on protein with and without stressed conditions still requires experimental proof. The interactions of a model protein hen egg white lysozyme (HEWL) and some homopeptides with sorbitol and a mixture of dodecyltrimethylammonium bromide (DTAB) + sorbitol] have been studied by using a combination of high sensitivity calorimetry, density, sound velocity, and conductivity measurements with spectroscopic support. The physical chemistry underlying these interactions has been addressed on the basis of the energetics of interactions and other physicochemical properties. These results have highlighted that, even though the number of –CONH groups increases in higher homopeptides, the hydrophobic effect of –CH₂ groups in the peptides dominates. Further, the counteraction of the deleterious effects of DTAB by sorbitol is due to the strengthened DTAB–sorbitol interactions rather than the indirect effect of the osmolyte via preferential exclusion. The results have provided insights into the nature of interactions of the protein as well as some of the building blocks with the (DTAB + osmolyte) mixture which helped in understanding the mode of action of the osmolyte. Detailed physicochemical insights into the mode of action of stress counteracting agents on the protein and its destabilizer are needed to develop strategies to achieve optimum stability and activity of proteins under such conditions.

Continuous Flow Synthesis: An Efficient Approach Towards Process Intensification

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Abstract:

Continuous –flow synthesis introduce advantages over batch synthesis in terms of efficient mixing of reagent substrates, shortened reaction (residence) times, thermal control, improved selectivity, mass transfer, batch to batch reproducibility, new chemistry space (high temperature solution phase synthesis), safety from hazardous chemicals, and inline purification. The key feature of the time efficient synthesis is automation and scalability in a safe and compact environment which enables on-demand and on-site chemical synthesis. In this poster presentation, I would present the recent work on Continuous flow synthesis in our laboratory. The work involves the scale-up of the organic molecules which requires the use of hazardous chemicals such as Butyl lithium, followed by the preparation of pentiptycene based organic molecules and polymers. The continuous process intensification of camphor production followed by the scale –up of the same is also under development in our laboratory. We have also developed a high-yield and high-throughput synthesis of polyaniline nanofibers through continuous flow process which exhibit high crystallinity, higher surface area and high specific capacitance.

Total Synthesis and Development of New Synthetic Methods

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Abstract:

Research in our group covers three major areas of synthetic organic chemistry: Total Synthesis, Asymmetric Catalysis and New Method development.

Total Synthesis: We have achieved the total synthesis of iso-crisamicin A, deoxycardinalin 3, asteriscunolide C, kalafungin, frenolicin B, phenatic acid, cephalosporolide H, murolic acid, paraconic acids, topsentolide B2, arizonins, etc.¹ Our recent focus has been towards developing highly efficient step-economic and protecting-group-free strategies to natural products such as Hagens' gland lactones, cephalosporolides E and F, cardiobutanolide, nephrosteranic, protolichesterinic, nephrosterinic, phaseolinic and rocellaric acids, muricadienin, ancepsenolide, etc.²

Asymmetric Catalysis:³ We have developed the π -allylpalladium chemistry and synthesized new pinene and menthane based catalysts for asymmetric allylation of imines. Our recent work has been in the synthesis of dimeric bis- π -allylpalladium catalyst that associate as dimers with four chloride bridges. We have also reported the unprecedented double arylation through π -allylpalladium formation by synergistic Pd(II) and Pd(0) dual-catalysis.

New Method Development:⁴ We have actively developed new terminal oxidants for Wacker oxidation, new ligands for several coupling reactions, tandem benzylic oxidation-dihydroxylation, Lewis acid catalyzed partial annulative dimerization and Bronsted acid catalyzed rearrangement of δ -hydroxyalkynones. Some of these methods have been extended toward the synthesis of natural products and new molecular scaffolds.

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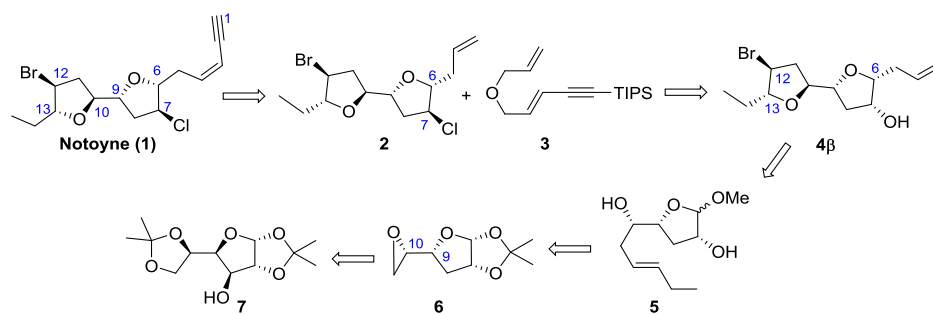
Total Synthesis of Notoryne & Related Diastereomers

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Abstract:

Notoryne belongs to a C15 Acetogenesis class of natural products that was isolated by Suzuki group from the leaves of *Laurencia nipponica* along with (3Z)-*Laurefucin* in the warm current region of Hokkaido at notoro point near Abashiri. The structure of Notoryne comprises a halo *bis*-THF unit along with an ene-yne unit. Laurendecumenyne B (one of the diastereomer of Notoryne) and the Elatenynes A/B are the other two closely related natural products. Structural reassignment are the common problems for such kind of natural products due to their conformational flexibility and overlapping NMR signals. There are several reports known for the synthesis of all acetogenesis except Notoryne. Taking these factors into account we planned our strategy to synthesis Notoryne.



Scheme 1. Retrosynthetic strategy of Notoryne

In this poster, presented will be the first total synthesis of Notoryne is completed from D-glucose as a chiralpool strategy. Bromoetherification, C-glycosidation and the relay enyne-metathesis were employed to build the key carbon-framework. The relative and absolute stereochemistry of Notoryne were assigned the by previous reports and by 2D NMR analysis. In addition, we have also synthesized four diastereomers of the Notoryne and analysed the ^1H and ^{13}C NMR spectra to arrive at some important information on how the C/H chemical shifts vary with respect to the relative stereochemistry of adjacent stereocenters.

Investigation of Novel Nano-structures for the Methanol Oxidation Reaction

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Abstract:

Over decades, direct methanol fuel cells (DMFCs) have received considerable attention among energy harvesting systems due to the unique possibility of direct conversion of fuel (methanol) into the electricity. Even though, lot of non-platinum based composite materials have been tried, Pt based catalyst are still prevailing in DMFCs due to faster oxidation of methanol on Pt. However, inherent tendency of Pt to get poisoned by adsorbed CO is holding back its commercial production in a bigger way. One way to surmount this challenge is to choose a novel supports/co-catalysts which will continuously provide hydroxyl groups for the oxidation reaction and will reduce the impact of poisoning. Furthermore, little attention has been given to develop specific electroanalytical methodology to probe CO adsorption reaction in a real time.

With this motivation, electro-catalytic oxidation of methanol on Pt nanoparticles loaded silica hollow spheres based electrodes was investigated in details. In spite of the poor conducting nature of the silica support, the oxidation potential and current density per unit mass for methanol oxidation were improved, substantially. This outstanding performance is attributed to the facile reaction between adsorbed CO on Pt with a surface hydroxyl groups present on hollow silica.

To monitor CO adsorption on electro-catalyst during methanol oxidation, novel fast scan cyclic voltammetry (FSCV) based method has been developed. To perform cyclic voltammetry measurements at higher scan rates ($\sim 10^4$ - 10^5 mV s⁻¹), Ultra-micro electrode (UME) geometries loaded with the catalysts has been employed. Peaks associated to CO adsorption have been elucidated as a function of scan rates. From that data, the average rate of CO adsorption in methanol oxidation has been quantified. This method can be generalize to any electro-catalysts of interest.

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Development of Novel Methodologies for the Synthesis of New Molecules and MaterialsSohan Lal,^a Irishi N. N. Namboothiri^{a*}^aDepartment of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India*Email: irishi@chem.iitb.ac.in**Abstract:**

Our group's research interests involve organic synthesis, development of new synthetic methodologies, asymmetric catalysis, mechanistic studies and materials chemistry. Cage compounds are a new class of potential HEDMs with severely strained molecular structures. These compounds have higher HoF and higher energy densities than traditional hydrocarbon fuels and our detailed investigation shows that newly synthesized compounds can be used as standalone fuels in liquid bipropellant systems, or as additives in liquid and solid propellants. The reactivity of nitroalkenes as substrates in the Morita-Baylis-Hillman reaction and applications of the Morita-Baylis-Hillman adducts in the synthesis of novel multi-functional and bioactive molecules, including heterocycles, have been investigated for the first time by our research group. The unexplored reactivity of the Bestmann-Ohira reagent and its sulfone analogs as 1,3-dipolar cycloaddition partners has been exploited by us recently in the synthesis of highly functionalized pyrazoles, including pyrazole alkaloid Withasomnine. The catalytic asymmetric synthesis of aminophosphonates, the transition state analogs of amino acids, and aminosulfones *via* Michael addition, application of Mg/CHBr₃ reagent system for 1,4-addition, 1,2-addition and cyclopropanation, stereoselective synthesis of carbocycles and heterocycles *via* cascade reactions involving curcumins and various Michael acceptors, synthetic and mechanistic studies on the vinylidenecarbene-acetylene rearrangement, application of carbon nanotube (CNT)-metal hybrids as heterogeneous catalysts in various organic reactions and Hauser-Kraus annulation of phthalides with nitroalkenes are other highlights of our research work. Detailed synthetic and mechanistic studies carried out by us have applications in areas as diverse as drug design, materials chemistry and asymmetric synthesis.

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